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THE ELECTRIC FURNACE

BY

HENRI MOISSAN.

AUTHORIZED TRANSLATION

BY

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AUTHOR'S PREFACE TO THE AMERICAN EDITION.

Since we commenced our first chemical researches with the electric furnace in 1892, we have found many reactions, one after another, which have been studied at high temperatures, both in the laboratory and in industry.

We have had the pleasure, since our first work, to see the development of certain industries, such as the preparation of calcium carbide, chromium, ferro-silicon, ferro-chromium, and ferro-titanium. At the same time, F. N. Acheson, who, in his discovery of the crystalline silicide of carbon, created the carborundum industry, and in pursuing the same, later was able to realize the industrial preparation of graphite. From various standpoints, attempts have been made to utilize the high temperature of the electric furnace in the manufacture of high grade steel, in glass-making, in the preparation of phosphorus, and in other industries. Frequently questions have arisen which later on resolved themselves into subjects for investigation for engineers. It is necessary to economically and continuously use a very high temperature which frequently causes action on the material of which the furnace is composed. During the past decade a large number of patents have been taken out in this direction and the perfection of electrical instruments, the ease with which currents of great intensity are handled to-day, the cheapness of their production near certain waterfalls, have aided in the development of numerous applications of the high temperature.

All these questions are now industrial studies. While the end of the scientific side has been far from reached, it must be remembered that the researches that remain to be realized become more and more exact, and the experimental study of this part of the science becomes more difficult.

Meanwhile we are continuing our experiments, and we hope later to add more to this interesting chemistry at high temperatures.

HENRI MOISSAN.

Paris, May 10, 1903.

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TRANSLATOR'S PREFACE.

The work of Professor Moissan with the electric furnace and the products obtained have been so far-reaching to the science of chemistry, and in particular, electrochemistry, that it has been deemed important to present an English translation of "Le Four Electrique."

The translator wishes to express his deep obligation to Professor Moissan for the additional matter in manuscript, which is included in this translation, thereby bringing the work up to date and also for his careful revision of all of the translation.

The translator also is indebted to Professor C. F. Burgess, of the University of Wisconsin, for valuable assistance in the examination of the proofs.

V. L.

INTRODUCTION.

The book is divided into four chapters:

In the first, we describe the different forms of electric furnaces which we have used in our work. We subsequently apply these apparatus to the study of the fusion and volatilization of a number of refractory substances.

The second chapter contains the study of the three varieties of carbon: amorphous carbon, graphite, and diamond.

The third chapter gives the preparation by means of the electric furnace of a number of elements. We describe the work done with the electric furnace on chromium, manganese, molybdenum, tungsten, zirconium, titanium, silicon, and aluminum.

The fourth chapter contains researches undertaken on a number of new binary compounds, the carbides, silicides, borides, phosphides, arsenides, and sulphides. We have shown the discovery of new compounds, giving their preparation, properties, and analysis. The preparation of calcium carbide, in particular, has been the subject of new investigation, which we repeat in some detail.

General conclusions complete the work.

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CHAPTER I

Description of the Different Models of Electric Furnaces

GENERAL REMARKS

The highest temperatures commonly attained in the arts are between 1700° and 1800°. In our laboratory furnaces we do not often attain, even with gas carbon, above 1500° to 1600°. Under these conditions, certain experiments become difficult to conduct, and scientific investigations find their limits in the fusion points of refractory clay and porcelain.

The use of the oxyhydrogen blowpipe by Henri Saint-Claire-Deville and Debray has rendered a great service to chemistry. Not only by means of this apparatus has it become easy to melt and refine platinum, to obtain new alloys, but as well to extend and generalize a number of problems in mineralogical chemistry.

The temperature which can be attained with this apparatus fed by illuminating gas and oxygen is about 2000°. According to Deville and Debray have found that lime alone can resist this Violle, the melting-point of platinum is 1775°. It is known that high temperature. Having had need, in my researches on the different varieties of carbon, to submit the metals to a higher temperature than 2000°, I thought to use the heat furnished by the electric arc.

The solution of the problem is theoretically very simple. It consists in placing in the smallest possible cavity, some distance above the substance to be heated, an arc of great intensity. The difficulties appear only when we attempt to incorporate these ideas into an easily handled and inexpensive form of apparatus. The forms of apparatus which I describe in this chapter are the first in which the action of the heat of the current may be clearly separated from electrolytic action.

Previous to our researches, various attempts had been made to use the high heat furnished by the electric arc. We mention in particular the work of Despretz which bears the title: *"Fusion et volatilisation des corps réfractaires. Note sur quelques expér-*

iences faites avec le triple concours de la pile voltaïque, du soleil et du chalumeau."[1]

Despretz utilizes more particularly the heat produced by the arc from a powerful battery.[2] We call attention in the different parts of this work to the results obtained by his investigation. In the investigations of Despretz and in that of similar workers, the material on which it is desired to act, is placed in the arc itself. Under this condition, the vapor of carbon and the impurities of the electrodes, which quite frequently are far from negligible, quickly come into play and materially complicate the conditions of the experiment.[3]

We find the same objection to many forms of the electric furnace used industrially. I need only to call attention to the furnaces of Siemens and Hutington, of Cowles, of Grabau, and of Acheson. In the first of these, the crucible forms one of the electrodes, and the current passing through the fused mass, makes it difficult to determine the part played by the action of the electric current and that due to elevation of the temperature by the arc.

Moreover, Siemens and Hutington worked in a carbon crucible. This being a good conductor, a large amount of heat is lost by radiation. This can explain why Siemens has obtained fused tungsten only in small quantities and with great difficulty.[4] This worker, in his English patents, says that a covering of quicklime can be used, but he appears not to have made many experiments in this direction, but he remarks on the difference of the results. Nevertheless, we should not forget that it is to Siemens and Hutington that we owe the first use of a practical electric furnace.

The furnace of Cowles answers very well for the particular industrial purposes for which it was devised, but the same objections can be made against it as against the Siemens furnace.

In the furnace of Acheson, a core of graphite, placed in the center of the material to be acted on, serves as a conductor and divides the current by forming, in the beginning, a large number

[1] *Compt. rend.*, **28**, 755 (1849).

[2] "Note sur la fusion et la volatilisation des corps," *Compt. rend.*, **29**, 48, 545, 712.

[3] The action produced by the impurities of the electrodes is frequently most important since small quantities of material are worked with and for only a short time.

[4] Siemens and Hutington: "On the Electric Furnace," British Association, Southampton, 1883 and *Ann. chim. phys.*, **30**, 465 (1883).

of smaller arcs with variable intensity. In place of an arc, a circuit is obtained in which the powerful heat of the current is not established in a regular manner until five hours after the beginning of the experiment.

These different forms of apparatus, used in the arts, are unhandy and little applicable to the many kinds of reactions in the laboratory, and frequently they cannot be used with currents of varying strength. I desired, on the contrary, to find a model of electric furnace for the laboratory which could be used for systematic and general use.

In the apparatus which we will describe, the arc possesses a great regularity during the entire length of an experiment and is very easy to handle. My electric furnace is not intended for industrial purposes. It is a research apparatus. It will therefore not be necessary to decide upon the results which could be furnished at the cheapest cost. Industrial requirements are that power shall be generated at a low cost and utilized with a high efficiency. As far as I have been concerned, I have not occupied myself with these questions. I have desired to enclose in as small a cavity as possible, an electric arc of great intensity in order to obtain the maximum temperature, and to illustrate my purpose I make the following comparison: In order to fill a reservoir having an outlet it is necessary to introduce water in much larger quantity than that which is lost by the outflow. Similarly the furnace, in order to reduce the loss to a minimum, should be made of a material which is the poorest possible conductor. For this purpose lime is quite suitable. To illustrate this, I give the following experiment: the dome of the electric furnace is formed of a plate of lime 3 cm. thick, under which the arc plays for ten minutes. The hand can be placed on this cover of lime whose outside temperature is not changed and whose inside surface is formed of a layer of several square decimeters of fused lime, which in the Drummond light gives such brilliancy that the eye cannot stand its intensity. A thickness of 3 cm. of lime arrests this enormous emission of heat.

The electric furnaces, which were used in our first work on the reproduction of the diamond, were modified little by little as the

subject grew, and we recapitulate in this chapter a series of simple and practical models, as follows:

1. Electric furnace of quicklime.
2. Electric furnace of calcium carbonate for crucibles.
3. Electric furnace for tubes.
4. Continuous electric furnace.
5. Furnace with multiple arcs.

Our first experiments, on the method of heating by the electric arc, were made with power derived from a 4 horse-power gas engine. The small dynamo which we used at this time was of the Gramme type. It gave a current of 35 to 40 amperes at 55 volts. In using a stronger current we pursued our work at the Conservatoire des Arts et Métiers, where the director, Colonel Laussedat, kindly placed at our disposal the resources of the institution. Under these conditions we have been able to use, for many years, a 45 horse-power steam engine, connected with an Edison dynamo. The current which could be obtained was 440 amperes at 80 volts. When we needed a stronger current we applied to the industries, and Fontaine of the Société Gramme very obligingly consented to lend us one of his dynamos run by a 100 horse-power engine. Later the *Compagnie des chemins de fer de l'Est* kindly placed at our disposal 60 to 100 electrical horse-power.

Finally, as we desired to push our experiments further, Meyer, director of the Société Edison, graciously offered the use of the central light station of Trudaine avenue, which every evening delivers 2000 horse-power. In many experiments we used 150 and 300 amperes for the object pursued, and it has seemed useless to go beyond this.

It is an agreeable duty to me, to present my sincere thanks to all who have been able to so kindly place at my disposal such means of research and who by this means have become my fellow-laborers.

Electric Furnace of Quicklime

Our first model of electric furnace, presented to the Academy of Sciences in December, 1892, was of quicklime.[1] It was com-

[1] Henry Moissan: "Sur un nouve an modèle de four électrique," *Compt. rend.*, 115, 988.

posed of two well-dressed blocks of lime laid one on the other. The lower piece contained a longitudinal groove through which passed the two electrodes, and in the center was a small cavity which served as a crucible (Fig. 1). This cavity can be of greater

Fig. 1. Plan of electric furnace.

or less depth and contains a layer of several centimeters of the substance which is to be heated by the arc. There can also be introduced a small carbon crucible containing the material to be heated. The upper block is slightly hollowed in the part which lies directly over the arc, and as the strong heat of the current soon melts the surface of the lime and gives to it a high polish there is formed a dome which reflects all the heat on the small cavity which contains the crucible. The electrodes are made easily movable by means of the supports which can be moved through two slits which work on stands. The difference between this furnace and those used heretofore, is that the material to be heated is not in contact with the electric arc; that is, with the vapor of carbon.

This apparatus is a reverberatory electric furnace with movable electrodes. This last point is of importance, as the moving of the electrodes gives an easy means of establishing the arc, for lengthening or shortening at will, and in a word, it materially simplifies the process of the experiment.

Arrangement of the Furnace.—In our first work, as we have already remarked, we used a small Gramme machine driven by a gas engine of 4 horse-power. Frequently the current which went through the furnace, indicated 35 to 40 amperes at 55 volts. Under these conditions, the lower block of quicklime measured 16 to 18 cm. long by 15 cm. wide and 8 cm. thick. The upper piece which joined the core had the same surface with a thickness

of from 5 to 6 cm. The dimensions of this furnace are quite sufficient for a current of 100 to 125 amperes and 50 to 60 volts. When it is desired to use a current of higher value the size of the furnace can be increased by enlarging each dimension 2 to 3 cm. With a furnace 22 to 25 cm. in length, it is possible to use the arc of a current of 450 amperes at 75 volts (Fig. 2). The lime used

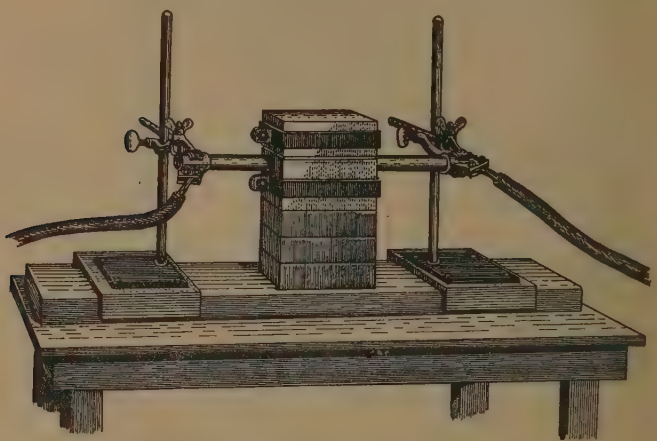

Fig. 2. Electric furnace for currents of 70 volts and 400 amperes.

in these experiments was slightly hydraulic, from the Paris basin and called *"du blanc vert"*. It is readily cut and turned. It is the same that Deville and Debray used in their small platinum fusions.

Electrodes.—The electrodes were formed of cylinders of carbon, as free as possible from mineral matter; we met some difficulties in the beginning of our work in obtaining them on the market in a condition of purity. These electrodes should be made of retort carbon selected from the top of the retort and reduced to a powder. The powdered carbon is treated with acid, in order to render it as free as possible from the iron which it contains. It is then washed and dried and finally cemented into a mass by means of tar. The cylinders are formed by a pressure

which must be very strong and very regular; finally they are carefully dried and baked at a very high temperature.[1]

An investigation should be made to determine whether for ease of manufacture boric acid or silicates have not been added to the carbon. We reject all carbon which contains these impurities and which contains more than 1 per cent. of ash.

For the small quicklime furnaces, we used electrodes 20 cm. long, and 12 mm. in diameter carrying 120 amperes at 50 volts, and cylinders 40 cm. long and 16 mm. to 18 mm. in diameter. When a 40 to 50 horse-power dynamo is used, electrodes are required 40 cm. long, and 27 mm. in diameter.

The extremities of the electrodes, between which the arc plays, were cut into pointed cones. This precaution is important especially with low currents since it is, at times, very difficult to relight the arc when it is extinguished at the beginning of the experiment. With a current of 350 amperes at 60 volts, we used only one electrode which terminated in a point. The end of the other was a plane. However, all difficulties vanish as soon as the furnace is hot, and when it is filled with the good conducting vapors, which allow the arc to play with greater ease.

The cables, which convey the current, are joined to the carbons by means of jaws of copper fastened by screws. This arrangement has been in use for a long time industrially for currents of high value.

Crucibles.—During the first part of our researches, we used crucibles of gas carbon which were made by turning out of a single piece. These crucibles have a cylindrical form; they have two notches placed at the extremities of the greatest diameter in order to allow the electrodes to pass through with ease.

With a 4 to 8 horse-power engine we used crucibles having an external diameter of 3 cm. and an internal diameter of 2 cm. Their height was 4 cm. and the notch was 1.5 cm. deep. These crucibles of retort carbon are inconvenient since they swell up and are transformed into graphite under the action of the heat of

1 In the beginning of these experiments, I used turned electrodes of retort carbon. Under the action of the arc, the ends of these electrodes enlarged into a fan shape, as the carbon was changed into graphite. This had already been observed by Despretz: *Compt. rend.*, 29, 716.

the arc. At our request several manufacturers made crucibles for us by pressure in a mold and obtained a single piece which maintains its form under the action of the highest temperatures. After the experiment it is found that a felt of fine graphite is formed which possesses rigidity.

It is well to preserve a vacant space around the crucible, so that the heat rays reflected by the top of the furnace completely envelop it. It must not be forgotten that lime is easily reduced by carbon at this high temperature, giving calcium carbide.[1] When a crucible is heated in this lime furnace it is necessary to be careful to pile up a layer of magnesia in the cavity of the furnace. The magnesium oxide is really the only known oxide that cannot be reduced by carbon. When the experiment lasts for a long time the magnesia melts, combines with the lime already liquid existing in the furnace, and volatilizes, but it does not give a carbide.

Performance of the Experiment.—Let us take, for example, the experiment which demonstrates the volatilization of quicklime. We do not need a crucible in the cavity since we operate on the material of the furnace. The experiment is begun by cutting a small hole 2 to 3 cm. deep in the lower block. The electrodes are then placed in the grooves and fastened by upright clamps which support the slides (see Fig. 2) finally brought to within 2 or 3 cm. of each other, the one being exactly above the center of the cavity. The current from the dynamo is then introduced into the circuit and when the second electrode is slowly moved toward the first, contact is established and the arc plays. Immediately a very penetrating odor of hydrocyanic acid is noticed. The small quantity of water, which is present in the electrodes, forms acetylene with the carbon. This gas in presence of the nitrogen which was present in the furnace at the beginning of the experiment, forms, under the powerful influence of the arc, the synthesis of hydrocyanic acid, discovered by Berthelot.

The light given off by the electric furnace, colored by the cyanogen flame, takes on a beautiful purple tinge which shortly

[1] H. Moissan: "Préparation d'un carbine de calcium cristallisé; propriétés de ce nouveau corps," *Compt. rend.*, **118**, 501.

disappears. Care should be taken at the beginning not to separate the electrodes too much, as when the furnace is still cold, the arc is easily extinguished. Some moments later it is different, and the arc can be slightly lengthened. At the beginning, the arc, and this is also true with high currents, is not 1 cm. in length while at the end of the experiment the arc is generally 2 to 2.5 cm. in length. If the furnace is filled with a metal vapor which is a good conductor (aluminum for example), the electrodes should be separated 5 to 6 cm. The size of tne arc is then regulated so that the same resistance is always obtained and the dynamo works normally, this regulation being effected by an ammeter and voltmeter.

With a current of 360 amperes at 70 volts, in three of four

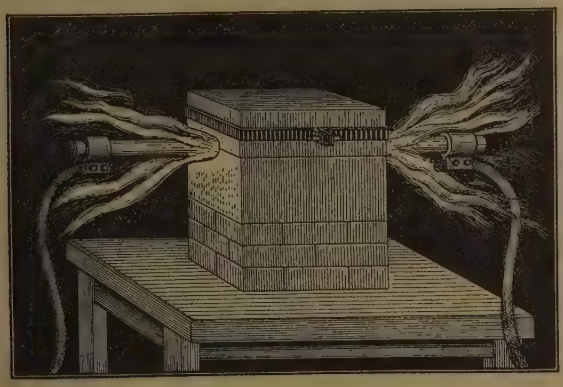

Fig. 3. Electric furnace in operation.

minutes, the electrodes become red; then brilliant flames 40 to 50 cm. in length sprout out of the openings which give passage to the electrodes on each side of the furnace (Fig. 3). The flames terminate in clouds of white smoke, which are produced by the volatilization of the lime and a portion can be easily condensed by deposition on a cold body. These vapors diffuse into the air and remain in suspension for many hours. With a current of 400 amperes at 80 volts an experiment can be completed in five or six minutes; by the use of a current of 800 amperes at 110 volts,

it is possible in five minutes to volatilize more than 100 grams of calcium oxide.

At the beginning of the heating, the arc possesses a certain variability and the furnace roars much, but in a short time, the metallic vapors increase the conductivity, the flow of the current becomes regular, and the operation proceeds without noise. The heat and light become very intense inside the furnace. When the experiment is concluded, the upper piece of lime is raised and it is noticed that the part which was under the action of the heat of the arc is completely fused. With a 50 to 100 horse-power dynamo, stalactites of fused lime are frequently formed on the cover which slowly trickle from the dome, and toward the end of the experiment solidify and present the appearance of wax.

The conductivity of quicklime is so poor that it is possible to place the hand on the outside while the inside has been raised to such a high temperature that it melts and gives an enormous quantity of heat and light by radiation. The poor conduction of the quicklime has been favorable to our experiments; it diminishes the loss of heat that we endeavor to confine in the smallest possible space. While magnesia is a much better conductor of heat than lime, when we attempted to construct an electric furnace entirely of magnesia, the results were less satisfactory. A furnace of the same form made entirely of carbon, but in which the electrodes were well insulated by means of tubes of magnesia, gave, by reason of its conductivity, an enormous loss of heat. After the experiments the positive carbons look as though they had been but little used while the negative is more or less deeply corroded. The extremities of the electrodes for about 8 to 10 cm. are entirely transformed into graphite.

When currents of a high tension are used, it is necessary to take certain precautions and to carefully insulate the conductors. When the furnace is in operation under the action of a 100 horse-power dynamo, the vapors which fill it are a good conductor of the current. It frequently happens that a secondary current is produced and successive shocks are felt by touching the supports or the electrodes. With a current of 30 amperes at 50 volts, such as used in the beginning of this work, the face should not be

exposed to a prolonged action of the electric light and the eyes should always be protected by spectacles of very dark-colored glass. Electric sunstrokes were frequent at the beginning of our work and irritation of the eyes, produced by the arc, causes a very painful congestion. It is particularly the low currents which produce this latter, since the heat being slight the operation of the furnace is watched.

In all our work we used a continuous current. There is another point to which too much attention cannot be called for the benefit of investigators or technical men who wish to repeat these experiments: When a furnace of limestone is used, a large quantity of carbon dioxide is liberated. This substance, in contact with the electrodes which are heated to redness and with a vapor of carbon, causes a continual evolution of carbon monoxide. The cylinders of carbon, which constitute the electrodes of the furnace, also furnish a small quantity. This gas does not burn completely and if great precaution for the ventilation of the room in which these experiments are carried on are not used, the operators soon begin to present symptoms of poisoning by carbon monoxide. Intense headaches, nausea, and general lassitude are experienced. It is necessary, under these circumstances, to quit for several weeks in order that this poisonous oxide of carbon may be completely eliminated.

The first model of electric furnace was used to study the crystallization of the metallic oxide, to prepare graphite which swells, to show the ready volatilization of platinum and the solubility of carbon in silicon, in platinum and in a large number of metals.

The difficulty of obtaining (especially in winter) large pieces of lime without cracks, and homogeneous, led us to quickly substitute calcium carbonate or building stone for the quicklime. Yet I still use this furnace to-day when I desire to avoid the abundant evolution of carbon dioxide. In the refining of certain metals, chromium for example, we still use this electric furnace.

Electric Furnace of Calcium Carbonate for Crucibles

As Deville and Debray have shown in their large platinum fusions, it is possible to substitute the quicklime by a piece of

Courson rock or by any other limestone containing little silicon.[1]

This calcium carbonate, of which the fine-grained is used, possesses the advantages of presenting a great solidity and of being readily obtained in sufficiently large pieces.

Arrangement of the Furnace.—The rock is cut into the form of a regular parallelipipedon, the size of which varies with the amount of current. For use with a 4 horse-power dynamo, the furnace should be made of two pieces, the lower of which is 10 cm. high, 18 cm. long, and 15 cm. wide. The cover has the same surface and has a thickness of 8 to 10 cm. For a 45 horse-power dynamo the dimensions should be the following: height of the lower piece 15 cm., width 20 cm., length 30 cm.; cover 11 cm. in height. With a 100 horse-power dynamo the height of the lower piece should be 20 cm., length 35 cm., width 30 cm.; cover 15 cm. high. A furnace of this description when properly handled can be used for seven or eight consecutive experiments. If greater power is used, the form of the furnace can be varied according to the experiment and as lime at these high tensions is volatile it is well to form the lower part of the furnace of a series of alternate layers of magnesia and carbon. Later on we will describe this last model.

It is very important to carefully dry the blocks of stone which are used in the furnace. For this purpose they are placed from twelve to twenty-four hours on top of a boiler or in the ashes of the hearth of a furnace or a hot-air stove. When the block of stone is well dried, it seldom splits under the action of the heat produced by the electric arc. In order to prevent this accident, we usually protected the furnace and cover by a metallic band, being careful to place it far enough away from the electrode so that a short circuit can not be produced. The lower parallelipipedon can also be placed in a case of sheet-iron of the desired size. Before drying, a cylindrical hole is cut in the center of the block larger than the crucible which is to be placed in it. Two apertures allow the sliding of the electrodes and their width depends on the diameter of the latter. The crucible is always placed on a

[1] Procès-verbaux de la Commission internationale du mètre. Esposé de la situation des travaux au Ier, Octobre, 1873, p. 9.

layer of magnesia in order to avoid the formation of calcium carbide, which, in a short time, renders it useless. It is well to allow 1 or 2 cm. space between the crucible and the side of the furnace in order that the strong heat may completely radiate around it.

When it is desired to condense the vapors of bodies difficultly volatile at a high temperature, we used a metallic tube cooled on the inside by a current of water. It is known that this arrangement furnished interesting results to Deville in his researches on dissociation. We used in these experiments a U-tube of copper 15 mm. in diameter, through which a current of water was allowed to pass under a pressure of one atmosphere. The curved portion of the U-tube was placed 2 cm. below the arc and above the crucible which contains the substance to be volatilized, and a sheet of asbestos board is placed next to the opening through which the cold tube passes, allowing the condensation of the metallic vapors which abundantly pass out of the furnace. The temperature of the water which passes through the copper tube is not raised more than 2° or 3°.

Electrodes.—The diameter of the electrodes naturally varies with the amount of the current. As we have shown in the furnace of quicklime, when more than 100 horse-power is used, cylinders of carbon are employed, 50 cm. long, and 4 cm. in diameter. For 200 to 300 horse-power, we used electrodes 5 cm. in diameter. In the last instance, the union of the flexible cables which convey the current of the electrodes, presents a slight difficulty. Care should be taken to avoid all contact which is not perfect, on account of the formation of an arc sufficiently intense to melt the clamp and the end of the cable. In order to avoid this, clamps of copper are used as is shown in Fig. 4.

Secure contact is insured by means of a metallic strip which is tightly fastened to the end of the electrode making many turns, and which is pressed by the clamp.

Crucibles.—We have already indicated the precautions to be taken in the manufacture of crucibles.

For a 45 horse-power engine, the crucibles are 6 cm. in diame-

ter, with a slope of 3 cm. When a current is used as high as 800 amperes at 110 volts, the internal diameter of the crucibles is 7.5 cm., the external diameter is 9 cm., and the external height is 10

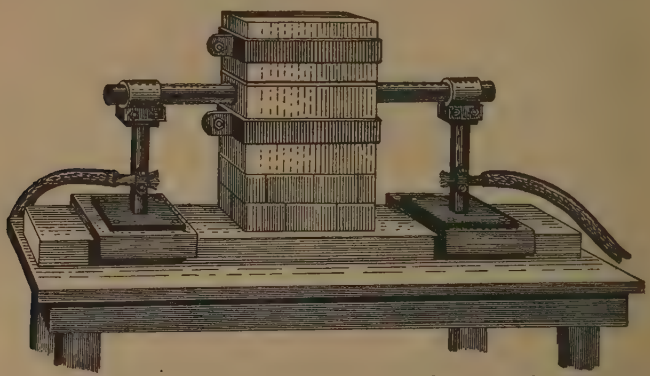

Fig. 4. Electric furnace with supports for currents of 110 volts and 1000 amperes.

cm., without slope. In these crucibles, it is possible to prepare in five or six minutes 300 to 400 grams of fused uranium or tungsten.

We also used magnesia crucibles of the same size. This magnesia was prepared with special care as previously shown.

Use of Alternate Layers of Carbon and Magnesia.—When a current having a tension of 1200 to 2000 amperes at 100 volts is used, the lime furnaces, if their cavity is not very large, are rapidly destroyed. By enclosing the intense arc produced by this current in a limestone furnace having a cavity whose internal diameter measures 10 cm., we obtained the following results: Fusion of lime flowing like water, volatilization of the latter in a short time giving volumes of smoke, roaring of the vapors through the openings through which the electrodes pass, continual cracklings produced by the small pieces of calcium carbonate which falls into the mass and are immediately dissociated, throwing out of the liquid lime, and finally raising of the cover under the action of the superheated gas and the vapors. Under these conditions, the experiment is not very easily managed. If the cavity in the furnace is enlarged, better results are obtained.

When it is possible to use these high tensions, it is well to make a cavity in the center of the stone, sufficiently large, having the form of a parallelipipedon and which contains alternate layers 0.01 m. thick of first magnesia, then carbon. These layers, four in number, are placed in such a manner that the magnesia is always in contact to the quicklime and the layer of carbon to the interior of the furnace. The magnesium oxide, not being reduced by the carbon, disappears only by volatilization, while at this high temperature the lime fuses in contact with the carbon, and easily forms liquid calcium carbide. The upper part of the cavity can be constructed in the same way of layers of magnesia and carbon, but more frequently it is sufficient to use a cover of rock having an elliptical depression 3 to 4 cm. in depth.

A furnace, constructed in this manner, can be used for many hours and consequently can be used for experiments which take a long time.

Preparation of the Magnesia.—The magnesia used in these experiments was prepared according to the directions of Schloesing.[1] It is necessary to purify this oxide from small quantities of impurities which it contains and which considerably lowers its fusion point. In order to accomplish this, basic carbonate of magnesia is heated several hours in a Perrot furnace. It is then reduced to a fine powder, and the magnesia which is obtained allowed to digest with an excess of a solution of ammonium carbonate; it is next washed well with water and finally ignited at the highest temperature of a good wind furnace. By addition of water a thick paste is formed with the magnesia which, by compression in wooden moulds, gives layers which are allowed to dry slowly. These plates are finally baked in a muffle.[2]

As Schloesing has shown, this magnesia contracts no further at the temperature of a wind furnace and undergoes no change under the action of atmospheric agents. Under the temperature of the electric furnace it contracts further, but under these conditions, it

[1] Schloesing: "Industrie de la magnésie," *Compt. rend.*, **101**, 131.

[2] This magnesia, to which a small quantity of water is added and strongly compressed in a hydraulic press, gives a very hard mass that scratches marble and fluorspar.

remains very light, taking on a crystalline appearance and increases in solidity.

Ditte has already shown[1] that under the action of heat, magnesia will easily polymerize and that it can increase from 3.193 to 3.569 in density. The magnesia of the layers of the electric furnace attains a density of 3.589 and that which has been fused 3.654. We have already shown that lime, fused or crystallized in the electric furnace, has the same density as that prepared at 800°.

The property of not being reduced, possessed by a magnesia, is possibly due to its polymerization.

The electric furnace of calcium carbonate has allowed us to perform our experiments with much greater rapidity. It is in this apparatus that I have been able to accomplish the production of the black diamond and the crystalline and transparent diamond, the preparation by kilograms and the refining of chromium, uranium, tungsten, molybdenum, zirconium, and vanadium.

It is in this that I have been able to bring silica and zirconia into the gaseous state, to distil these substances, to show by the heat of the arc the volatilization of copper, aluminum, gold, iron, uranium, silicon and carbon. It is also in this furnace that I have been able to prepare, with ease, the silicide of carbon, the boride of carbon, the boride of silicon, the carbides of calcium, barium and strontium in crystalline form, the carbide of aluminum, and the various crystalline borides and silicides.

Electric Furnace for Tubes

The arrangement of the furnace for crucibles which we have described permits the heating of sufficiently large quantities to a high temperature, but it is impossible to avoid, with this model of furnace, the action of the gas which fills the apparatus. During the entire duration of the experiment, the carbon dioxide which is produced on account of the decomposition of the calcium carbonate is largely transformed into carbon monoxide. The water which is always found in the limestone, in spite of drying as completely as possible, constantly gives a mixture of hydrogen and carbon monoxide.

[1] Ditte : "De l' influence qu' exerce la calcination de quelques oxydes métalliques sur la chaleur dégagée pendant leur combinaison," *Compt. rend.*, **73**, 111 and 270.

In order to avoid the action of these gases in certain reactions we constructed our electric furnace in the following manner: A piece of the fine-grained rock (as free from silica as possible) is cut into the form of a parallelipipedon having a height of 15 cm., a length of 36 cm., and a width of 25 cm.

The internal walls of the cavity are constituted of alternate layers of magnesia and carbon, in the manner previously shown; the cover is constructed of a block of the same material. Finally, a carbon tube passes through the furnace and the lateral plates perpendicular to the electrodes. Its internal diameter can vary from 5 to 40 mm.; it is placed 1 cm. below the arc and 1 cm. above the bottom of the cavity.

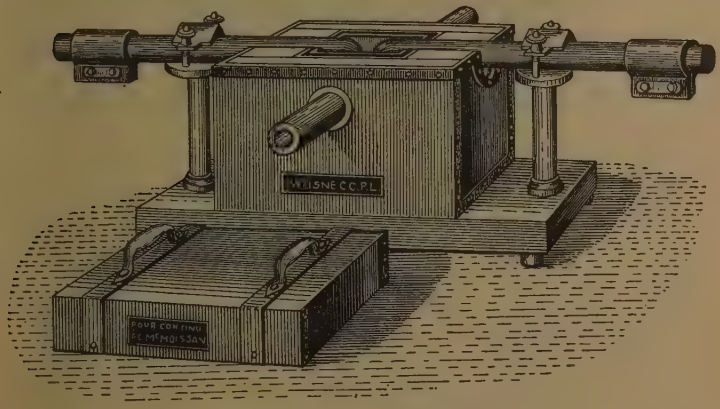

Fig. 5. Furnace with horizontal tube

The apparatus, arranged in this manner (Fig. 5) can be heated for many hours with currents which vary from 300 amperes at 70 volts to 1000 amperes at 60 volts. The part of the carbon tube which is exposed to this high temperature, is entirely transformed into graphite. But if the tube is of pure carbon, and it does not touch the lime[1] and if it has been carefully made under a strong pressure, the graphite forms a felting, and the diameter of the tube does not change.

1 The electrodes and the tube are separated by a thin layer of magnesia.

In different experiments we placed the tube above the arc, but under these conditions the temperature is not as high.

In order to avoid the direct action of the carbon on the substance undergoing the experiment, the carbon tube can be lined inside and outside with magnesia. The experiment then is limited, it is true, by the volatilization of this oxide; but attaining this degree of heat, a large number of interesting studies can be made.

It has not been possible to use any other materials than carbon in the construction of the horizontal tube. All substances found in nature, or which can be made in the laboratory, fuse and volatilize before carbon. These carbon tubes present the serious inconvenience of being considerably porous. We have endeavored to avoid this as much as possible by using double tubes or tubes covered by magnesia. All attempts made of fusing on their surface a cover of silicide of carbon, boride of carbon, or other carbides, have been fruitless; we nevertheless pursued this study, but it would be very desirable for the delicate studies which remain to be attempted at elevated temperatures to obtain a perfectly tight tube. These carbon tubes are closed at their ends by stoppers of moulded magnesia or cut pumice stone. These stoppers were provided in the center with round holes for the introduction of glass tubes. These different parts fit into each other with gentle friction and a tight seal is effected by means of a luting of magnesia and alkaline silicate.

When it is desired to place the substance to be heated in boats, a carbon tube having a diameter of 4 cm. and a length of 50 cm. is used. It is possible under these conditions to fuse and volatilize various substances in a current of nitrogen or hydrogen with greatest ease. Nevertheless the gas currents used in these experiments should be very rapid and the gases should be dried with the greatest care. This style of furnace we used in the beginning of a study on some gaseous reactions at the high temperature furnished by the electric arc. We hope later on to publish the results of the delicate experiments which we pursued in this line.

It is by means of this electric furnace that we have been able to

prepare crystalline carbide of silicon, pure and colorless, by the direct union of the vapor of carbon and the vapor of silicon. This apparatus we used in the studies on the crystalline borides of iron, nickel and cobalt, in the preparation of zirconium, pure carbide of aluminum, carbide of titanium, the carbides of the cerite metals, and in the study of the various nitrides. It is particularly useful for the preparation of a compound in a definite gas.

Continuous Electric Furnace

The above-described apparatus contains a horizontal carbon tube; if the tube be inclined 30°, the furnace is transformed into an apparatus for the preparation of refractory metals, a continuous apparatus in the center of which can be slid the mixture of oxide to be reduced and carbon, while the liquid metal flows down the inclined plane. In this continuous electric furnace, as well as in the electric furnace with a tube, I have completely separated the electrolytic action from that of the thermal action.

With a current of 600 amperes at 60 volts, it is easy to obtain, in an hour, a lump of fused metallic chromium of about 2 kilograms. The metal was collected in a hollowed-out piece of limestone lined with chromium oxide. The metal remains liquid for some time, loses all the gas which it contained in solution and begins to undergo the process of refining. A mass is thus obtained which, after solidification, appears as a white and very hard metal, with a fine grain, capable of taking a high polish.

Furnace with Multiple Arcs

In the experiments which it is possible to undertake by means of the electric furnace, two possible cases can appear:

(1) If it is necessary to attain a very high temperature, a powerful arc is enclosed in the smallest possible cavity. This is the case in the furnace of lime or the crucible furnace that we have already described. Under these conditions the heat rapidly acts on the sides of the furnace; the lime or magnesia fuses and rapidly volatilizes. With currents of 1200 amperes at 110 volts, the apparatus is rendered useless in ten or fifteen minutes.

(2) If it is desired to produce a considerable quantity of a metal which is formed at a high temperature, we should make a larger cavity in the electric furnace and use the heat gradually as it is produced, continuously giving it work to do. In this second instance, the furnace with an inclined tube, or the furnace having a bottom, should be used.

It is very often possible to form a bottom sufficiently refractory to support the metallic liquid which is obtained, and in this case, for regulating the heat on a large surface we divide our current into a number of arcs.

In using a bottom which is slightly inclined, it is possible to introduce in the higher part an intimate mixture of the oxide with carbon. Under the action of one or two arcs, the metal is formed, fuses on the bottom, and accumulates on the lower part where another arc keeps it liquid while it is refined. The liquid can be allowed to flow out by a hole which is opened at the end of the operation. In an experiment made on a small scale we were able to obtain, at one time, 10 kilograms of fused chromium. In another experiment, we obtained 12 kilograms of fused molybdenum. The intense heat, produced by the electric arc, can therefore be applied in a continuous furnace, and gives, in this case, a regular production of metal whose fusion point can be above 2000°.

In concluding the description of the different models of electric furnaces which we have used in our work, there is yet an important point to which attention should be called.

We have ignored the temperature of these apparatus; it depends on the temperature which can be obtained by the electric arc and which, according to Violle, is 3500°. This is a matter on which opinion can differ, as for us, after making hundreds of experiments under widely different conditions, it has seemed that in a closed furnace, with a small cavity, the temperature rises with the amount of the current.

It is likely that the vaporization of carbon can, in a certain measure, limit the temperature of the arc, when currents are used which are not very high; in the same way the phenomenon of the depolymerization of carbon, which occurs, also complicates the thermal conditions of the experiment. But it always appeared in

the many investigations made, and in studies undertaken with widely differing currents, that the more we increased the power, the more the temperature increased. With 400 amperes at 70 volts, it was possible to reduce vanadium oxide by carbon, the crucible being placed in an arc of 1 cm. With a current of 1000 amperes at 70 volts, this reduction is made with a large arc, and about 100 grams of metal were obtained in a few minutes.

The reduction of titanic acid by carbon furnishes us a striking example of the increase of the temperature as a function of the intensity of the current. With an arc of 50 amperes at 50 volts only the blue protoxide of titanium is obtained whatever the length of the experiment may be; an arc of 350 amperes at 50 volts gives us the fused nitride and nothing but nitride; finally, with a current of 1000 amperes at 70 volts, this nitride is completely dissociated and liquid titanium containing more or less carbide is obtained.

Conclusions.—Many experimenters have hitherto used the electric arc to obtain high temperatures, but those who have preceded me, have not separated the electric action of the current from the thermal. It is this separation which I desired to make by taking up only the powerful thermal action that the arc furnishes and leaving outside the purely electrolytic action.

The electric furnaces which I have described are simple and practical pieces of apparatus and explain much of the chemistry of high temperatures. The services which they can render in the laboratory and in industry could be very great. These apparatus have allowed us to readily attain temperatures bordering on at least 3500°; it is then particularly these studies which are to be pursued, and the first results obtained show the importance of, and extent to which these investigations can be carried in this direction.

Crystallization of the Metallic Oxides

We first applied our electric furnace entirely to the study of the crystallization of the metallic oxides, then to volatilization of some of the elements.

In order to study the action of a high temperature on the metallic oxides, the electric furnace of quicklime previously described was used. The oxides were prepared pure and anhydrous.

The powdered oxide was packed in the center of the cavity below the electrodes, and the arc allowed to play. For the first part of these investigations, that is to say, in those where a 4 horse-power dynamo was used, the carbon electrodes were previously submitted to the action of chlorine at a high temperature, then cooled in a current of nitrogen. In the experiment where a 35 to 45 horse-power was used, we employed as electrodes cylinders of carbon which were as pure as possible, and which were prepared with the minutest precautions. When an intense current is used, the reactions can be made on quantities sufficiently large that the small quantity of impurities in the electrodes do not strongly influence the results of the experiment.

Calcium Oxide.—When lime is submitted to the action of the arc produced by a current of 25 amperes at 50 volts, the mass is soon covered with brilliant, white crystals of pure calcium oxide.

These crystals can be obtained in small quantities by means of oxyhydrogen blowpipe in the portion heated the highest, that is to say, near the jet of the blowpipe.

If, for pure lime, there be substituted a lime slightly hydraulic such as forms the material of the furnace, good crystallization is produced.

These crystals have a density of 3.29; they are readily soluble in water and on analysis show the following composition:

Lime	97.30
Alumina	1.60
Silica	0.45
Iron	trace

Although the lime used was very rich in alumina and colored yellow by iron, the crystals obtained were completely colorless, and were similar to those which St. Meunier and Levallois, in a continuous lime furnace, heated by gas.[1]

If a stronger arc is used, 100 amperes at 50 volts, the crystallization becomes more abundant and rapid, but when an arc of 250 amperes at 70 volts is used the mass fuses and the crystallization of the fusion is indistinct. Under these conditions the cavity enlarges, the two blocks of lime themselves fuse, and the experiment is limited by the fusion of the material which constitutes the

[1] St. Meunier and Levallois: *Compt. rend.*, June 28, 1880.

furnace. Pure lime, free from silica, alumina, or magnesia, fuses well, and rapidly.

After fifteen or twenty minutes, when a furnace of ordinary size is used, the external walls are heated to bright redness and the experiment should be brought to an end.

If a tension of 110 volts and 1,200 amperes is used, the fusion and volatilization of the lime is energetically produced in a short time. In five minutes it is possible to volatilize several hundred grams of lime. If the experiment is stopped, the top of the furnace is covered with a layer of fused lime, 2 or 3 cm. thick, having a crystalline fracture. The fused part has a milky, transparent appearance, and its density is 3.12 at 18°. Similar results are obtained when a furnace of calcium carbonate is used. The arc soon forms an oval cavity in the fused lime covered by a white layer of lime 2 cm. thick. If a considerable quantity of alumina is added to the lime, its fusion point is lowered and its fluidity is much increased.

Fused lime presents an unexpected resistance to hydration. In three jars containing distilled water we placed: (1) Lime from marble; (2) fat lime of good quality; (3) pieces of fused lime.

The lime from marble immediately slakes and the liquid when tested with ammonium oxalate gives a white precipitate. The fat lime soon swells and goes very rapidly into solution in water. Twelve hours later it is complelety slaked. On the contrary, the fused lime does not change in appearance after twenty-four hours' contact with water, and the liquid contains no trace of lime in solution. It must remain forty-eight hours before a sensible enlargement is observed, and then lime water is formed.

Boiling water gave a series of similar reactions. We can conclude from these experiments, that calcium oxide, as long as it is not hydrated, is insoluble in water, and that fused lime resists the action of water much longer than ordinary quicklime. Air saturated with moisture at the temperature of the laboratories gives the following results: Lime from marble is completely slaked in twenty-four hours; fat lime in forty-eight hours; and fused lime does not change its waxy appearance until after forty-eight hours; after three days, it still contains some particles which are not hydrated.

The experiments were made under a bell-jar supported in a large crystallizing dish containing water, and the small pieces of lime were placed in cups which floated on the liquid.

We observed the same gradation in treating the different specimens with acids.

Strontia.—Strontium oxide crystallizes like lime under the action of an arc of 75 amperes at 50 volts. With a current of 350 amperes at 70 volts, pure strontium oxide fuses to a transparent liquid, which, on cooling, becomes a confused crystalline mass. Strontium oxide fuses easier than lime.

Baryta.—Baryta, as is known, melts at a lower temperature than lime. With an arc of 25 amperes at 50 volts, it becomes liquid; it is readily volatilized under the action of an arc of higher intensity. On cooling, liquid baryta gives a mass of tangled crystals which show a good crystalline fracture.

Magnesia.—Magnesia crystallizes at a higher temperature than lime; it gives bright crystals which sometimes are several millimeters long. The experiment succeeds very well by working with an arc of 120 amperes at 50 volts above a mass of pure magnesia placed in the center of an electric furnace. When 360 amperes at 70 volts is used, the magnesia forms a milky and translucent fused mass.

Ditte demonstrated in 1871 that magnesia is polymerized by successively raising the temperature and that its chemical and thermal properties similarly vary. Particularly the density of this oxide rapidly increases with the temperature. Ditte has given the following figures:

	Density at 0°.
At 350°	3.1932
At dull redness	3.2482
At white heat	3.5699

In our experiments, made in the electric furnace, we always observed that magnesia purified by the method of Schloesing was not reduced by carbon. The knowledge of this property was very important to us, since it has enabled us to construct the interior of our furnace of alternate layers of magnesia and carbon, and to use magnesia in the construction of crucibles.

In view of the ready reduction by carbon at the temperature of

the arc of the alkaline earth oxides, alumina, and uranium oxide, this stability of magnesia has seemed curious enough to us to cause us to investigate the density of the oxide fused in the electric furnace.

These determinations were made in benzene and in absolute alcohol according to the precautions of Ditte in his paper.[1] Each of the figures given below represent the mean of four determinations.

The first sample was heated for ten hours in a wind furnace heated by retort carbon. The second sample was from the plates of magnesia and was partially crystalline. It had been heated for two hours by the electric arc. The third was taken from a mass of 50 grams of magnesia fused into a single piece in a crucible in the electric furnace.

We obtained the following figures:

	Density at 20°.
1. MgO (wind furnace)	3.577
2. MgO (blocks of the furnace)	3.589
3. MgO (fused mass)	3.654

This increase in the density indicates that the polymerization of magnesia continues up to its melting-point. The density can vary between 3.19 and 3.65.

Alumina.—In order to study the action of the arc on pure alumina, the latter is placed in a carbon crucible in a lime furnace. It is impossible to operate on a small quantity of alumina placed in a lime furnace. Under these conditions a liquid calcium aluminate rapidly forms. With an arc of 25 to 30 amperes at 50 volts, the alumina fuses and crystallizes rapidly on cooling. If a small quantity of chromium sesquioxide is added, small red crystals of ruby can be separated from the mass. These rubies are not so good as those prepared by Fremy and Verneuil; but the rapidity of the experiment which lasts only ten or fifteen minutes, makes possible the preparation of crystalline rubies. Probably the easy volatilization of the alumina would allow good crystals to be obtained by this means. We have not followed this study further.

When the arc is more powerful, as from the current of 250 amperes at 75 volts, and the experiment is continued twenty minutes, the alumina not only fuses, but volatilizes so completely

[1] Ditte: "De l'influence qu' exerce la calcination de quelques oxydes métalliques sur la chaleur dégagée pendant leur combinaision," *Compt. rend.*, **73**, 111 and 191.

that nothing remains in the crucible. This permits the repetition in several minutes of the famous experiment of Ebelmen on the synthesis of corundum by the volatilization of boric acid in a porcelain furnace.

When the experiment is very short, three to five minutes, the crystallization is indistinct and the crystals lose their brilliancy.

With an arc of 300 amperes at 60 volts, fused boric acid is completely volatilized in a few minutes.

Oxides of the Iron Group.—Chromium sesquioxide, heated with an arc of 30 amperes at 55 volts, fuses and gives a black, shining, knotted mass, containing small, dark-colored crystals which, on treatment with potassium nitrate and precipitation with mercurous nitrate, gave the following results:

		Found.		
	Theoretical	I.	II.	III.
Chromium	52.22	51.82	51.60	52.32
Oxygen	47.78	....	....	....

These crystals are very hard and show a green streak on porcelain. Chromium sesquioxide, when fused, combines rapidly with calcium oxide. In the lime furnace, in which chromium was refined, hundreds of grams of this well-crystallized double oxide were obtained. Similar brilliant and leaf-like crystals were sometimes found on top of the furnace.

We have been able to prepare many of these double oxides by heating a mixture of quicklime and chromium sesquioxide in varying proportions in a limestone furnace, with a current of 1000 amperes at 50 volts. The fused mass, when removed from the furnace, frequently shows geodes containing small, transparent, yellow-colored, crystal plates, which are slowly decomposed by water or moisture. The compound contained only lime and chromium oxide. On analysis they have the following figures:

		Found.		
	Theory for $Cr_2O_3.4CaO$.	I.	II.	III.
Chromium	27.2	26.9	26.8	27.6
Calcium	41.1	41.4	42.5	...

They consequently appear to agree to the formula $Cr_2O_3.4CaO$. Near these yellow plates we frequently found dark green needles several millimeters long, but have not studied them.

Manganese dioxide, under the action of the arc, rapidly fuses;

it boils with evolution of oxygen and gives liquid protoxide which is absorbed by the lime, forming a brown-colored, crystalline mass, which probably consists of a combination of the two oxides.

Iron sesquioxide rapidly fuses and loses part of its oxygen. Magnetic oxide, Fe_3O_4, is formed as a liquid and becomes partially crystalline.

This oxide, like chromium sesquioxide, readily forms crystalline combinations with lime. These compounds are produced with such ease that it has always been impossible to melt iron in the small cylindrical lime crucibles heated on the bottom by an oxyhydrogen blowpipe. The magnetic oxide which is formed under these conditions unites with the lime; the latter becomes brown, softens, falls together and allows the liquid which it contains to run out. After the experiment has been completed, the entire bottom of the crucible has been transformed into a double oxide of calcium and iron.

Nickel peroxide forms a fused mass covered with small, green, transparent crystals.

Cobalt protoxide, which also fuses very rapidly, forms rose crystals.

Titanic acid, under the action of a current of 25 amperes at 50 volts, forms well-defined, prismatic crystals, dark in color, which correspond in appearance and properties to the lower oxide of titanium.

If a current of 100 amperes at 45 volts be used, this peroxide first fuses, after heating three minutes, is partially dissociated, and at the end of eight minutes is completely volatilized.

All of the experiments described were made on the oxide not in contact with carbon and the mass was heated several centimeters from the arc, in order to avoid the reducing action of the carbon vapor.

Copper Oxide.—Copper oxide is completely decomposed in the electric furnace; it gives small particles of metallic copper and a crystalline double compound of oxide of calcium and oxide of copper.

Zinc Oxide.—Amorphous zinc oxide is volatilized in a few moments and forms transparent needles several centimeters in length, which deposit on the apertures of the furnace and on the carbon electrodes.

Conclusions.—At a temperature slightly above 2000°, lime has sufficient vapor-tension to allow good crystals to form. When the heat of the electric arc is above this, the lime melts and the liquid, on cooling, takes on a crystalline form. Under the action of a higher temperature, the lime boils and readily distils.

Strontia and baryta crystallize and melt at lower temperatures.

Magnesia, below its melting-point, gives vapors which condense into bright crystals. With a great elevation of temperature, it fuses, but with greater difficulty than lime, and finally passes into a state of vapor.

Alumina is more readily volatile than lime or magnesia. It is, therefore, readily apparent why, in the ordinary wind furnace, it is possible to volatilize alumina and obtain crystals of corundum. On fusion, a crystalline mass is formed to which a trace of chromium gives a ruby color.

In the electric furnace, boric acid, titanium protoxide, and zinc oxide are rapidly volatilized. Copper oxide is dissociated into oxygen and into copper which distils.

The oxides of the iron group, stable at high temperatures, give fused masses covered with small crystals. In all of our work, a simple elevation of temperature has been sufficient to effect the crystallization of the metallic oxides.

Since our first work in this line, Dufau made a study on the crystallization of oxides, by means of the electric furnace, and has shown the existence of a chromite of calcium, Cr_2O_3,CaO; of a tetrachromite of barium, $4Cr_2O_3,BaO$; of a cobaltite of magnesium, $MgCoO_3$; and of a nickelite of barium, $BaO,2NiO_2$.

Finally, on applying the same method to the crystallization of the sulphides, Mourlot has reproduced alabandite or sulphide of manganese, previously obtained in the wet way by Baubigny and in the dry way by Gautier and Hallopeau. He also prepared the sulphides of chromium, zinc, cadmium and aluminum.

Fusion and Volatilization of Some Refractory Bodies

We dwell more particularly, in this chapter, on those experiments which show the volatilization of some of the metals and non-metals, and on the ready distillation of silica and zirconia. In order to condense the vapors of these refractory bodies, volatile at a very high temperature, we used a metallic tube cooled on the

inside by a current of water, which we described in our electric furnace of limestone for crucibles. As an example of the use of the cold tube, we mention the action of heat on two stable compounds in inorganic chemistry; namely, the pyrophosphate and the silicate of magnesium.

Magnesium pyrophosphate was submitted, for five minutes, in the electric furnace to the action of an arc of 300 amperes at 65 volts. After a short time, a large amount of vapor was given off. A current of water having a temperature of 15.4° was passed through the cold tube placed in the furnace before the experiment. At the end of the operation and at the time when the furnace was in full operation, the temperature of the water which was passed from the tube was only 17.5°. Under these conditions, the vapors which are formed in the center of the furnace are readily condensed on the cold tube. When the latter was withdrawn from the furnace, we found it partially covered with ordinary phosphorus which, inflamed by friction, or slowly oxidized in the air, gave a syrupy covering which strongly reduced silver nitrate. Besides the phosphorus, we detected the existence of magnesium on the tube.[1]

In another experiment we heated asbestos (magnesium silicate containing a little iron) in a carbon crucible for six minutes. The current measured 300 amperes at 75 volts. After the experiment, there remained only a very small quantity of the fused silicate in the crucible and a small ferruginous globule having a bright fracture and containing 1.6 per cent. of magnesium and 0.7 per cent. of silicon.

The cold tube was covered with a gray powder, containing a large quantity of silica, magnesia, and small quantities of carbon and silica. We also found spherical particles of transparent silica, which scratched glass and gave the characteristic reaction for silica in a salt of phosphorus bead.

These two preliminary experiments, which we picked out from many others, demonstrate that the most stable salts are dissociated

[1] There remained in the crucible, a gray, porous, fused mass which, on analysis, gave, for phosphoric acid and magnesia, very different figures from those on the pyrophosphate used :

	Pyrophosphate.	Fused mass.
Phosphoric acid.....	63.96	43.84
Magnesia.....	36.04	55.58

at the temperature of the electric arc, and that it is possible to collect and study the decomposition products.

A. Volatilization of Metals

Copper.—A piece of copper weighing 103 grams was placed in a carbon crucible in the electric furnace. It was heated five minutes with a current of 350 amperes at 70 volts. After a minute or two, brilliant flames, 0.40 to 0.50 meter long, played with force from the openings through which the electrodes pass in each side of the furnace. These flames terminated in clouds of yellow smoke produced by the formation of copper oxide, from the combustion of metallic copper. After the experiment had been continued for five minutes the current was stopped. The fused mass which remained in the crucible weighed only 77 grams. Under these conditions, 26 grams of copper were volatilized.

Around the crucible in the horizontal part which lies between the cover and the furnace there was found a large golden circle of fused copper globules from the distillation of the metal. The yellow vapor collected gave up copper oxide when treated with dilute hydrochloric acid in the cold, leaving a residue of small spheres of metallic copper, black on the surface and soluble in nitric acid.

Silver.—It has been known for a long time that silver is volatile at a high temperature. In the electric furnace, it is possible to boil silver. It distils with greater ease than silica or zirconia. A large quantity of fused globules were obtained as well as an amorphous gray powder, and arborescent particles.

Platinum.—Heated in the electric furnace, platinum fused and in a few moments was volatilized. The metal was collected in small bright globules, and as a powder on the cooler part of the electrodes or on the surface of the lower block a few centimeters from the crucible.

Aluminum.—Heated for six minutes with a current of 70 volts and 250 amperes a gray coherent powder was obtained on the cold tube, which, when shaken with water, broke up into small spheres of aluminum which settled to the bottom of the vessel. These spheres had a metallic appearance and were attacked by hydrochloric or sulphuric acid with evolution of hydrogen. From the

vapors which escape from the furnace, it is possible to collect, on an asbestos board, small spheres covered with alumina.

Tin.—Length of experiment, eight minutes. Strength of the current, 380 amperes at 80 volts. When the furnace is in full action, there is an abundant evolution of white smoke around the electrodes. On the tube is found a small quantity of tin oxide soluble in dilute hydrochloric acid, and small, white globules of gray substance having a fibrous appearance and forming a felt. The fibrous portion and the metallic spheres, when treated with hydrochloric acid, gave an evolution of hydrogen; they were metallic tin. It is easy to condense small particles of metallic tin mixed with oxide on the outer part of the furnace.

Gold.—Length of experiment, six minutes. Strength of the current, 360 amperes at 70 volts. 107 grams of gold were placed in a crucible; after the experiment there remained but 59. During the experiment, large quantities of a yellow-green-colored smoke were evolved. The cold tube was covered with a dark-colored powder with a purple reflection. Under the microscope, with a low power, small regular spheres of fused gold having a beautiful yellow color could be distinguished. These globules were readily soluble in aqua regia and the solution gave the characteristic tests for gold.

When the vapors of the furnace were condensed on an asbestos board, at the highest heated portion, numerous, small globules of metallic gold were formed. Around this portion, which was pure yellow, there was a band of red, and farther away a beautiful, dark purple color.

Manganese.—This metal, of which the volatilization has recently been shown by Jordan, gives very interesting results. We describe here only one experiment that appeared characteristic. Length of heating, ten minutes; strength of current, 380 amperes at 80 volts. 400 grams of metallic manganese were placed in the crucible. During the experiment, much smoke was evolved, and at the end, we found a lump of metallic carbide weighing a few grams. Moreover, in each case in the preparation of manganese in the electric furnace, too long heating left no metal in the crucible.

Iron.—Length of experiment, seven minutes. Strength of cur-

rent, 350 amperes at 70 volts. There was obtained on the cold tube, a thin gray, lumpy powder possessing some bright faces, malleable enough to yield under a knife blade, mixed with a gray powder, having the color of iron reduced by hydrogen. This powder became bright by burnishing, and a sample was completely soluble in dilute hydrochloric acid with evolution of hydrogen.

On the asbestos board where the metallic vapor was condensed, small spheres of the magnetic oxide and black globules of the same compound having a rough surface were obtained.

Uranium.—Length of experiment, nine minutes. Strength of current, 350 amperes at 75 volts. On the cold tube there was obtained a large quantity of small metallic spheres, mixed with a deposit of gray powder, which was readily soluble in acids with evolution of hydrogen, the solution giving all the characteristic tests of uranium salts. On the asbestos board, there was found a large quantity of yellow spheres which, crushed in an agate mortar, lost their crust of oxide, became gray, and took on a metallic appearance. These spheres of distilled uranium do not contain carbon and are not attracted by the magnet.

B. Volatilization of the Non-Metals

Silicon.—With a current of 300 amperes at 80 volts it is possible to volatilize silicon. On the cold tube, are formed small spheres of fused silicon, which are attacked by a mixture of nitric and hydrofluoric acids. These spheres are mixed with a gray powder and a small quantity of silica. If the vapors are condensed on an asbestos board, it is observed that a large part of the silicon has been transformed into silica. It is possible to show this volatilization of silica by the arrangement shown on page 7.[1]

Crystalline silicon prepared by the methods of Deville or Vigouroux was placed between the two vertical electrodes. When the arc was allowed to play, there could be easily seen, by means of a projected image, the silicon beginning to fuse, then to boil. Where the electrodes cooled, there was found on the end surrounded by the graphite formed, light green crystals of carbon silicide.

Boron.—It is not possible to volatilize boron from a crucible in the electric furnace since, under these conditions, it is transformed

[1] See also H. Moissan: "Reproduction du diamant," *Ann. chim. phys.*, 8, 466.

into carbon boride. When pure amorphous boron prepared by means of magnesium[1] is introduced and the experiment projected, as above mentioned, the boron was observed to become red, then become surrounded by a large green ring, and disappear without fusing.

After the experiment there was found on the ends of the electrodes small black masses having a fused appearance, showing some crystalline points which were formed by carbon boride of definite composition.

In the experiment it is necessary to have the carbon electrodes as pure as possible. It should not be forgotten that with a large quantity of boron, along with the compound of boron and carbon, boric acid can appear. It quickly melts and boils but can be easily removed by boiling water.

From this experiment it can be concluded that boron passes from the solid to the gaseous state without becoming liquid.

Carbon.—Length of experiment, fifteen to twenty minutes. Strength of current, 370 amperes at 80 volts. On heating, under these conditions, a crucible filled with large pieces of carbon near the arc, the whole mass was transformed into graphite and after the experiment very light translucent layers of chestnut-brown color were observed on the cold tube. Berthelot, in his numerous experiments on the progressive condensation of carbon, has shown the existence of a light carbon of a chestnut color. This material was separated from the lime that had been volatilized along with it, by dilute hydrochloric acid. The residue, thus obtained, burned readily in oxygen with the formation of carbon dioxide. Later on, we will study in more detail the properties of this vapor of carbon.

C. Oxides

The experiments previously described on the crystallization of the oxides completely demonstrate the volatility of these compounds; such oxides as lime, magnesia, and zirconia need only be mentioned.

Lime.—With a current of 350 amperes at 70 volts, lime can be volatilized in eight to ten minutes. With these conditions, there is obtained, on the cold tube, lime which has the form of an amor-

[1] H. Moissan: 'Preparation du bore amorphe,'' *Compt. rend.*, 114, 392.

phous powder, but does not show little spheres. Large quantities of the vapor of calcium oxide issue from the furnace. With a current of 400 amperes at 80 volts, the experiment is completed in five minutes. Finally, with a current of 1000 amperes at 80 volts, it is possible to volatilize in five minutes more than 100 grams of calcium oxide.

Magnesia.—Magnesia is more difficult to volatilize than lime; besides, its boiling-point is close to its melting-point. When magnesia is fused, it gives off vapors which can be condensed on the cold tube. This experiment is made with a current of 360 amperes at 80 volts. The distillations become very pretty and very rapid when a current of 1000 amperes at 80 volts is used.

Zirconia.—When zirconia is submitted to the high temperature of the electric furnace, the oxide quickly fuses. At the end of ten minutes, when a current of 360 amperes at 70 volts is used, large quantities of white fumes are evolved. These fumes are formed by the vapor of zirconia for at this high temperature the zirconia is boiling. By condensing these vapors on a cold body, a white powder is obtained which is treated with a large quantity of dilute hydrochloric acid to remove the lime which it contains. After treatment with boiling water and drying, a white powder remains which, under the microscope, shows white, rounded masses, containing no transparent particles. This powder exhibits all the characteristics of zirconia. It scratches glass readily and has a density of 5.10. After cooling, the crucible is found to contain a mass of fused zirconia, which shows a crystalline fracture. Inside the furnace, in the portion which had been the least heated, characteristic crystals of zirconia were sometimes found. They resembled transparent dendrite, had a vitreous luster, scratched glass, and were not attacked by sulphuric acid. A crystalline combination of lime and zirconia also exists.

Silica.—Pieces of quartz, placed in a carbon crucible, were submitted to the action of the electric arc produced by a current of 350 amperes at 70 volts. In a short time, the silica commences to fuse and in seven or eight minutes begins to boil. A blue smoke, lighter than that produced by zirconia, is seen coming from the apertures of the furnace, through which the electrodes pass. While the experiment continues, these vapors are abundantly

evolved. They can be condensed by placing an inverted crystallizing dish some distance from the opening in the furnace. The interior becomes rapidly covered with a light layer of a substance which is not very transparent, and is of a light blue, white color. On treating the contents of the crystallizing dish with water, and on examining this residue with a magnifying glass or microscope of weak power it is seen to be formed of opalescent spheres, which are readily soluble in hydrofluoric acid. These little spheres of silica (Fig. 6), visible to the naked eye, are plentiful; they sometimes exhibit in a portion, a hollow part seeming to indicate that fused silica contracts on passing from the liquid to the solid state. Along with these spheres, a large number of particles of amorphous silica were found.

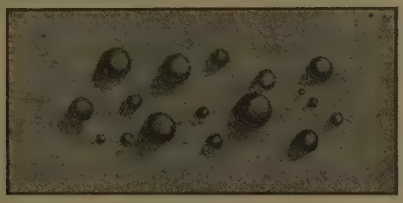

Fig. 6. Spheres of silica.

To prepare this product in quantities, it is better to use a furnace whose cover has a vertical opening above the crucible, allowing the vapors of silica to pass out. A glass bell-jar or metallic receiver is placed over this opening (Fig. 7), when it is possible to obtain, in ten or fifteen minutes, 20 grams of a very light, white powder which is purified from the contaminating lime by treatment with dilute hydrochloric acid. The form of the condensed silica naturally depends upon the rapidity with which the vapor is cooled. The cooling should not be too rapid when a quantity of spheres of silica are desired. This silica is easily soluble in hydrofluoric acid, dissolving in the cold with a slight hissing noise. It is easily attacked by fusion with potassium hydroxide and by the alkaline carbonates. Its density is 2.4 which is less than that of quartz; these little spheres easily scratch glass.

By studying the deposit formed in the glass globes around an electric arc lamp, we found spheres of silica similar to those

described here. It is particularly to this volatilization of the silica that the glass globes of the arc lamps, which have been used for some time, owe their opalescence. This silica comes from the

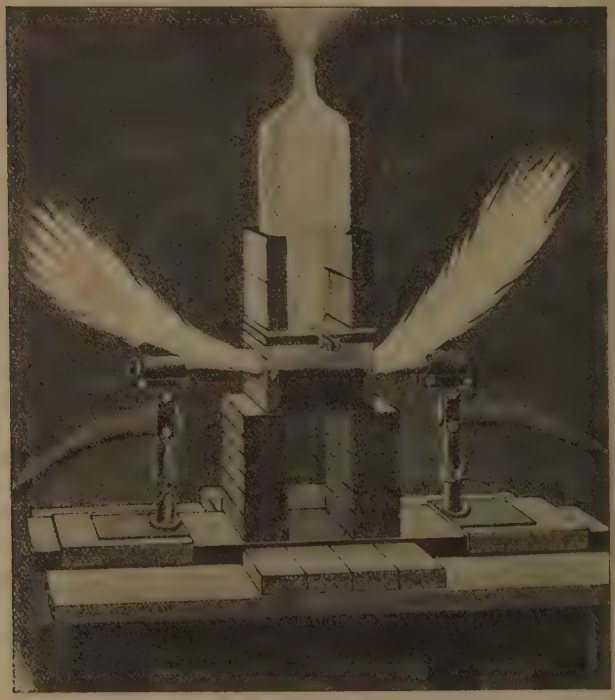

Fig. 7. Electric furnace arranged for the volatilization of silica.

impurities of the carbon electrodes. We would mention that silica, at this temperature, is easily reduced by carbon, giving a crystalline silicon carbide, as does pure silicon.

Zirconia and silica rapidly fuse in the electric furnace and after seven or eight minutes they pass by boiling into the gaseous condition.

Conclusions.—At the high temperature produced in our experiments by the electric arc, the metals and non-metals, which are commonly regarded as refractory, are volatilized. The most

stable compounds in inorganic chemistry disappear in the electric furnace either by dissociation or by volatilization. There is, however, a new series of perfectly crystalline bodies which have an exceptional stability that we will describe later.

They are the metallic borides, the silicides and especially the carbides.

CHAPTER II

The Various Modifications of Carbon

FIRST PART

Amorphous Carbon

Of all the elements, carbon occurs in the most curious allotropic forms. The opposite properties and the differences of the specific heat of diamond, graphite and lampblack, have for a long time attracted the attention of chemists. After separating and studying the laws of the animal and vegetable kingdoms, the chemistry of carbon has produced a large number of new compounds. It has taken such a range that it is possible to use the remark of Berthelot, "Chemistry creates the objects for its researches." But in the imposing array of researches, chemists themselves are attached to the production of certain derivatives, new syntheses, some of which have found industrial application, rather than to the extension of our knowledge of the properties of simple bodies which serve as the starting-point. The hypothetical form of the carbon atom is frequently discussed while there exist but comparatively few experiments on the physical and chemical properties of this same carbon. This subject deserves further study.

In order to prepare the artificial diamond we have made a general review of the work on the different varieties of carbon. We give here a review of the subject treating successively of amorphous carbon, graphite and diamond. First we deal with amorphous carbon. It is known that the properties of this variety of carbon can vary within wide limits. The resistance to oxidation, for example, has been studied by Ditte.[1]

In comparative experiments he showed that the varieties of carbon, when heated in a sealed tube with a concentrated solution of iodic acid, are attacked at different temperatures.

After some experiments made with iodic acid, permanganate of potassium, chromic acid and nitric acid, we prefer as a means of

[1] Ditte: "Recherches sur l'acide iodique," Thèse de la Faculté des Sciences de Paris No. 322, 1870.

oxidation, a mixture of sulphuric acid and potassium bichromate.

Different chemists have been occupied with the preparation of amorphous carbon. Among the work undertaken on this subject we recall in particular that of Gore,[1] who showed that carbon was insoluble in carbon dioxide, in cyanogen, and in liquid hydrochloric acid. He studied the action of sulphide of carbon on silver, lead and mercury, at ordinary temperatures. He tried as well the action of a voltaic couple, formed of sheets of platinum and aluminum on the hydrocarbons and on organic compounds. In most cases there was no decomposition.

It is known that amorphous carbon can form in a number of decompositions, as in the action of metallic sodium or magnesium on carbon dioxide. Winkler[2] studied more particularly the action of magnesium on the alkali and alkaline earth compounds; he showed the formation of amorphous carbon under these conditions without dwelling on the properties of the bodies obtained. In the same order of ideas comes the study of Dragendorff on the liberation of carbon by the action of phosphorus on the fused alkaline carbonates,[3] as well as that part of the work of Gore, in which he describes the action of phosphorus on fused cyanide of potassium.

It is also seen that in these reactions the heat evolved is great. We are not concerned with the carbon obtained under these conditions; on the contrary, all our efforts have been directed to a study of the liberation of carbon at a temperature as low as possible and in very slow reactions.

The brilliant work of Berthelot on the different states of carbon, the theory of the pyrogenic carbides, the synthesis of acetylene by the vapor of carbon, and on the humic acids, constitutes the most important work hitherto made on this subject.

COMMERCIAL LAMPBLACK.—The lampblack which we studied was produced by the decomposition of petroleum by heat. The temperature of its formation, which is quite irregular, is for the most part of the mass little above a low red heat. We took this point as the comparison in the study of amorphous carbon.

[1] Gore: *Chem. News*, **50**, 125 (1884).
[2] C. Winkler: *Ber. d. chem. Ges.*, **23**, 2642 (1890).
[3] Dragendorff: *Chem. Centrbl.*, Nov. 20, 1861, p. 865.

The material was purified by successively treating it with benzene, alcohol, and ether. This purification is necessary as the quantity of hydrocarbons contained is considerable. After washing with ether, the dry black powder was placed in a drying oven and the temperature slowly raised to 150°.[1] The lampblack floats on iodide of allyl having a density of 1.87 and sinks in propyl iodide whose density is 1.78. Lampblack thus prepared is far from pure. It retains with great tenacity small quantities of the hydrocarbons, and water which it is impossible to remove. It contains as well a little nitrogen.

In order to make an analysis of this variety of carbon, it is first heated in a vacuum to the point where ordinary glass softens, in order to polymerize it and render it easier to handle. It evolves water and traces of hydrocarbons. The black powder gave the following figures:[2]

	I.	II.
Ash	0.22	0.34
Carbon	93.21	92.86
Hydrogen	1.04	1.20

If we calculate the hydrogen as water we find that we exceed 100 per cent. which seems to indicate that a small quantity of hydrogen, less than 1 per cent., without doubt exists as hydrogen; the remainder appears as water which it is impossible to completely remove from the lampblack. If it is not dried in vacuum and at a low red heat, the quantity of water is much greater. The crude material gave, on analysis, the following figures:

Carbon	87.49
Hydrogen	2.76

If the hydrogen is calculated as water, there is obtained:

$$C\ 87.49 + H_2O\ 24.88 \quad 24.88 = 112.37.$$

This total hydrogen 2.76 is both the hydrogen existing as water and as combined hydrogen. The latter appears as organic matter probably in the form of a hydrocarbon. This constant presence, in amorphous carbon, of hydrocarbons, hydrogen, and other simple bodies, has been known for a long time. We recall numerous examples. Berthelot has drawn from these facts the following conclusions:

[1] This treatment with alcohol and ether should be prolonged to eliminate the last traces of benzene which the lampblack retains.

[2] Two analyses were made on different samples.

"In reality, the carbon cannot be regarded as a real element; on the contrary, it resembles a highly condensed hydrocarbon, with unusually little hydrogen and an unusually high molecular weight. In a certain measure, pure carbon means a border state that can be reached only by the highest temperature that we can produce. As known in the free state, it represents the extreme border of molecular condensation, that is to say, a state removed as far as possible from that of the element carbon, brought into a gaseous condition and comparable to hydrogen. This explains why carbon never separates at a low temperature, contrary to hydrogen and the most of the elements.[1]

When the composition of this lampblack was determined, experiments were made on samples purified by solvents and not heated.[2] When heated with a mixture of 100 grams sulphuric acid and 16 grams of potassium bichromate, the lampblack is attacked at 60°. At this temperature, a slight boiling in the mass is observed, produced by the carbon dioxide which is evolved. The experiment is made by introducing about 0.01 gram of lampblack into a glass tube 1 cm. in diameter, in which has been placed 2 cc. of the oxidizing mixture. The top of the tube is drawn out and bent into a reversed U-shape and dipped into a small test-tube which contains a clear solution of barium hydroxide. When the evolution of gas begins, the baryta water becomes clouded. This little apparatus is placed in a glycerin bath and a thermometer is placed beside it. The temperature of combustion in oxygen was determined by means of the pyrometer of Le Chatelier and is 371°.

Lampblack, thus purified, has enabled us to establish the influence of temperature on the polymerization of this body. To this end the following experiments were made:

1. The lampblack was heated for five minutes in a small porcelain crucible, by means of a blast-lamp, to 910°. After heating, it was not attacked by the chromic acid mixture at 90° and began to burn in oxygen at 440°.

2. It was heated at the same temperature for three hours. The material obtained began to be attacked by the chromic acid mix-

[1] Berthelot: "Théorie des corps pyrogénés," *Ann. chim. phys.*, 4e série, 9, 475.

[2] Berthelot has shown that lampblack contains a trace of graphite due to the combined influence of heat and oxidation. Berthelot: "Recherches sur les états du carbon," *Ann. chim. phys.*, 4e série, 19, 392.

ture at 95°, and the temperature of combustion in oxygen rose to 476°. Its density was 1.87.

3. After being heated for six hours, the lampblack was attacked by the chromic acid mixture at 99° and burned in oxygen at 506°.

Therefore the polymerization of carbon, under the action of heat, for a constant temperature, is not instantaneous, but depends on the length of time of heating.

Amorphous Carbon Obtained by the Incomplete Combustion of Acetylene.—The ready production of acetylene from fused and crystallized calcium carbide, the preparation of which has been shown in the electric furnace, has permitted the formation of this hydrocarbon in a sufficiently pure state to prepare amorphous carbon. The acetylene gas is allowed to burn at the ends of glass tubes having a diameter of 6 mm. Above each flame, is placed a cylinder of copper 3 cm. in diameter, which is cooled by the passage of a current of cold water. Lampblack forms on the metal in large masses resembling mushrooms.

Under the microscope, this carbon does not show a homogeneous color, some parts being more or less brown; when it is heated, it loses some volatile products, and on treatment with benzene, a small quantity of carbon compounds is extracted. It contains a little nitrogen but not as cyanides. This carbon is purer than the lampblack of commerce. The purification of this specimen was effected by successive extractions with benzene, alcohol and ether. The properties of this amorphous carbon are quite similar to those of lampblack; it is attacked by the mixture of sulphuric acid and potassium bichromate at a temperature of 92°. In oxygen, its temperature of combustion is 375° and its density 1.76. Heated to dull redness in a vacuum it lost no volatile hydrocarbons; it lost water and then gave the following analysis:

Ash	0.12	0.80
Carbon	92.71	92.53
Hydrogen	0.96	1.00

The amorphous carbon obtained by the incomplete combustion of acetylene is consequently purer than the ordinary lampblack; but its analysis shows that it also retains some water which does not go off at a low red heat.

Amorphous Carbon Obtained by the Explosion of Acet-

YLENE.—Berthelot has shown that acetylene gas can be suddenly decomposed into carbon and hydrogen by means of a small charge of mercury fulminate.[1]

Thanks to Vioille, we have been able to prepare a considerable quantity of this amorphous carbon. This carbon contains not only traces of hydrogen, but also a small quantity of lead, from the cartridge used in the explosion. Under the microscope this carbon has a beautiful black color. It gives on analysis:

	Found.		
	I.	II.	III.
Ash	7.21	7.51	8.03[2]
Carbon	92.30	92.61	92.52
Hydrogen	0.41	0.40	0.40

Outside of the quantity of lead which it contains, this variety of amorphous carbon is purer than any we have studied. It contains very little hydrogen and was carefully treated with reactive liquids. It does not lose carbon compounds with acids, alkalies, or hydrocarbons. It contains no trace of nitrogen. It is attacked by the different oxidizing agents at the following temperatures:

Potassium permanganate (6.5 grams to 100 H_2O)	98°
Commercial fuming nitric acid	80°
Pure fuming nitric acid	106°
Chromic acid mixture (as before)	98°

Combustion takes place in oxygen at 385°.

We thus see the result of the influence of temperature and possibly of pressure on amorphous carbon. It is attacked by the chromic acid mixture and burns in oxygen at a higher temperature than the carbon obtained by the combustion of acetylene in the air.

ACTION OF SULPHURIC ACID ON STARCH.—When fuming sulphuric acid is allowed to act on starch at 200° for twenty-four hours, a black substance is obtained, which is purified by washing with cold water, alcohol and ether.

The black powder is homogeneous under the microscope, but is not pure carbon. It is organic matter, richer in carbon than the

[1] Berthelot: "De la force des matières explosives," Vol. I, p. 109.

[2] These analyses, like the preceding, show that amorphous carbon is not absolutely homogeneous.

humic acid obtained by Berthelot and André.[1] It shows by its partial solution in alkalies, that it is only a decomposition product, a step toward the element carbon. This black material dried at 400° gave, on analysis, the following figures:

Ash	2.64
Carbon	73.69
Hydrogen	2.29

If the black residue obtained by the decomposition of sugar by fuming sulphuric acid be heated in the air, a large part of the organic matter is destroyed and a less impure carbon is obtained.[2] It actually contained:

Ash	4.26
Carbon	88.21
Hydrogen	0.75

But as the impure carbon is already polymerized by the action of heat, it is of no interest to us.

Action of Ferric Chloride on Anthracene.—When pure crystallized anthracene is heated with a saturated solution of ferric chloride to 180° in an apparatus having a reflux condenser, decomposition takes place. After treatment for twenty-four hours, a dark chestnut-colored powder is formed which, on drying, becomes black. After many successive treatments with hydrochloric acid, then with boiling water, the substance is finally extracted with benzene, alcohol, and ether; this latter treatment, if continued a long time and repeated, removes the most of the hydrocarbons, which the powder retains with the greatest energy. The product, thus prepared, is a mixture of ferruginous organic matter, which, on heating, gives volatile products. Analyses gave the following figures:

Ash	21.29
Carbon	62.17
Hydrogen	0.91

Here also we obtain a transition carbon compound. Examined under the microscope, the material is not homogeneous; there are particularly found fine needles which are easy to distinguish and

[1] Berthelot and Andre have studied the black material which is produced by the action of the boiling, concentrated hydrochloric acid on sugar. They obtained a humic acid which contained 63–64 per cent. carbon. Berthelot and Andre: *Ann. chim. phys.*, 6e série **25**, 364 (1892).

[2] This carbon always retains some sulphur, which becomes an integral part of the molecule.

which were formed by the chloride of Julin (C_6Cl_6). The ash is very rich in iron sesquioxide, the metal taking part in the combination. This preparation does not furnish pure carbon.

Action of Heat on Carbon Tetraiodide.—Pure crystalline carbon tetraiodide was prepared by the action of boron iodide on carbon chloride.[1] Carbon iodide heated to 200° in a vacuum decomposes into protoiodide, iodine and a black substance, which, examined under the microscope, is amorphous. At first sight, this black amorphous powder might be taken for a variety of carbon, but it is not; it is the combination of the iodide and carbon which again goes to show how difficult it is to separate carbon at low temperatures from those substances in which it is found combined. Analysis gave 45.44 per cent. carbon but no hydrogen. We recall that the decomposition of the fluorides of carbon, at red heat, produced a lampblack.[2]

Decomposition of Carbon Tetraiodide by Light.—We have shown in previous work that under the action of light, the carbon tetraiodide loses iodine and forms a new iodide, C_2I_4, which we have called carbon protoiodide. When this experiment is made with well-dried tetraiodide and in vacuum, the decomposition into iodine and protoiodide is effected under the action of light, in three or four weeks. It is complete and no carbon is set free. If the tube contains a small quantity of water, the decomposition becomes more complex, and a black amorphous product is obtained which is not a form of pure carbon; it contains traces of hydrogen and a considerable quantity of iodine.

Action of the Smithson Pile on Carbon Protoiodide.—This experiment was made in the following manner: A Smithson pile, formed of a strip of tin which was surrounded by gold foil, was placed in a solution of carbon tetraiodide in sulphocarbonic acid. The tube which contained the liquid was drawn out, filled with carbon dioxide, exhausted and sealed.

The experiment was begun in August, 1892, and ended on the sixth day of May, 1896, lasting four years. On the surface of the tin, beautiful crystals of tin iodide were found, and on the gold leaf a slight deposit of a black powder. Under the microscope, this deposit was absolutely amorphous. It had a chestnut color,

[1] H. Moissan: "Étude du tétraiodidure de carbone," *Compt. rend.*, **113**, 19, July 6, 1891.
[2] H. Moissan: "Fluorures de carbone," *Compt. rend.*, **110**, 951.

and was readily attacked by nitric acid. It was uniformly deposited on the metallic plate and appeared to have limited the electrochemical action by its poor conductivity. The quantity obtained was too small to allow an analysis to be made or to measure the temperature at which it was attacked or at which it burned. It is probable that the body thus obtained was not pure carbon. Nevertheless, it was completely insoluble in the acids, except in concentrated nitric acid, or in the hydrocarbons, and treated with a 25 per cent. solution of potash gave no coloration.

In this experiment, which was conducted at the ordinary temperature and under the slow action of a very feeble electrolytic decomposition, the black residue which was deposited took on an amorphous form; it is to this point that we have mainly directed our attention. Berthelot has already described the formation of amorphous carbon in the slow combustion of cuprous acetylide at ordinary temperature.[1]

Decomposition of Carbon Tetraiodide by Zinc Filings.— In a glass tube, prepared as we have already shown, were placed zinc filings and a sulphocarbonate solution of carbon tetraiodide. The experiment was begun in August, 1892, and ended in May, 1896. At the instant the tube was opened, the liquid was colored yellow, indicating a transformation of the tetraiodide into the protoiodide. The metallic filings were covered with a layer of dark brown color. After washing with carbon disulphide, the metal was dissolved in very dilute hydrochloric acid; a gas was evolved having an odor resembling that of the sulphines, and there remained a powder having a brown-black color. The residue was suspended in water, collected, and washed with alcohol, pure benzene, and finally again with 95 per cent. alcohol. This material dried at 100°, appeared in the form of black amorphous powder, very light, yielded nothing in hot benzene, and was insoluble in a boiling potash solution, or in hydrochloric acid.

This powder, in its appearance and properties, much resembles that obtained by means of the Smithson pile. It burned readily on platinum foil, leaving a slight residue of zinc oxide.

Action of Some of the Metals on Carbon Tetraiodide.— At the same time that the preceding experiments were made, a number of tubes were prepared under similar conditions. They

[1] Berthelot: "Recherches sur les états du carbone," *Ann. chim. phys.*, 4e série, 19, 392.

contained a sulphocarbonate solution of carbon tetraiodide, in presence of sodium, silver, lead, mercury, and magnesium. The substances were all allowed to act for four years. The sodium, silver, mercury, and lead all reduced the tetraiodide to protoiodide, without setting free carbon. Magnesium, only, gave a different result. The metallic filings used in the experiment were covered with a slight brown-black deposit, which, on treatment with cold dilute nitric acid, was set free as a fine powder that swam on the surface of the liquid.

Under the microscope, the material appeared amorphous and dark brown in color; when burned in oxygen it gave carbon dioxide and contained no traces of iodine or magnesium. It completely enveloped the magnesium filings, forming a felt which appeared to arrest the decomposition. I believe that this method of setting free carbon can be attributed to an electrochemical action, analogous to that of the action of the Smithson pile and arises from the non-homogeneity of the magnesium filings. At all events, this carbon, slowly deposited on the magnesium filings, possessed all the properties of the more readily attacked carbon. It was very light, soft and absolutely amorphous.

Carbon Obtained by the Reduction of Carbon Dioxide with Boron.—Pure boron was introduced into a tube of Bohemian glass, and a current of well-dried carbon dioxide passed over it. When a dull red heat was attained, the boron burned with evolution of light in the carbon dioxide. A black, porous powder was found and when this was washed with water, amorphous carbon remained. This powder was treated with chlorine gas at a low red heat to remove the last traces of boron, and finally washed with water and dried.

The carbon was obtained at a high temperature and in a reaction where hydrogen was not present; it was pure, but was already polymerized and was attacked with difficulty. With the oxidizing mixture it gave carbon dioxide at 80° and burned in oxygen at 490°. Its combustion can be compared with that of ignited lampblack. The carbon was fairly pure; analysis gave:

Ash	0.96
Carbon	86.16
Hydrogen	1.41

or ash, 0.96 + C 86.16 + H_2O 12.70 = 99.82.

Conclusions.—We have undertaken a study of the known forms of amorphous carbon. We have purified lampblack and have demonstrated that its polymerization under the action of heat is not instantaneous and that it increases with the time. This polymerization raises its temperature of combustion in oxygen and increases its stability in presence of an oxidizing mixture of chromic and sulphuric acids.

Following this we studied the amorphous carbon produced by the incomplete combustion of a definite hydrocarbon such as acetylene and that produced by the explosion of the same hydrocarbon under slight pressure. The latter is the more stable. These different varieties of carbon were produced by reactions which set free considerable heat. We endeavored to prepare carbon at a low temperature.

The action of sulphuric acid on starch and of ferric chloride on anthracene only gave rise to organic products; the final decomposition products were black compounds, richer in carbon than the humic acids prepared by Berthelot and André. The decomposition of carbon tetraiodide, when heated to 180°, gave a black powder, rich in iodine, an intermediate product between the original compound and carbon. This experiment supports the theory advanced by Berthelot on the decomposition of organic bodies by heat. The slow action of the Smithson pile on carbon protoiodide in sulphocarbonate solution gave a small quantity of a dark brown powder insoluble in caustic potash, but readily attacked by concentrated nitric acid. Zinc filings acting on carbon tetraiodide gave rise to similar results.

Finally, we studied another variety of carbon, produced by the decomposition at dull redness of carbon dioxide by boron. The density of the purest lampblack, which has not been ignited, is 1.76. These experiments fully demonstrate how difficult it is to obtain pure amorphous carbon.

When carbon is produced at the ordinary temperatures and pressures, it is obtained as an impalpable powder having a dark brown color. It is very light and soft, and is readily oxidized by nitric or chromic acid. This carbon always retains a certain amount of other elements such as hydrogen, iodine, lead, zinc, etc., owing to their presence in the various reactions. If an attempt

be made to eliminate these impurities by heat the carbon is polymerized. All kinds of amorphous carbon retain water with great tenacity. Whatever the method of preparation of these kinds of carbon, whether it be formed slowly or rapidly, whether it be made in the cold or at a low red heat, whether the product be pure or impure, it is always soft, its density is below 2, and it is always amorphous.

SECOND PART.

Graphite

Before the work of Berthelot, graphite was not defined as a definite thing. In early times all the varieties of carbon which, by friction on paper, made a bright gray mark, were given the vague name, graphite. At this time molybdenite was confounded with graphite. By applying the reaction of Brodie to the analysis of a mixture of the different varieties of carbon, Berthelot was able to define graphite as "that variety of carbon which, on oxidation, is capable of forming graphitic oxide."[1]

This property definitely establishes the classification of carbon into three groups: Diamond, graphite, and amorphous carbon, including all the varieties which occur in nature or which can be prepared artificially. Graphitic oxide is usually prepared, according to the method of Brodie, by allowing graphite to come in contact with the oxidizing action of a mixture of potassium chlorate and nitric acid. It appears as a crystalline compound which possesses the property of deflagrating on the application of heat with increase of volume, and leaving a black residue of pyrographitic oxide.[2] Berthelot carefully described the condition of this oxidation and applied it to the study of known graphites. I have extended this study to some natural graphites and to numerous samples of the graphite which I have obtained in my studies on the chemistry at high temperatures.

When fuming nitric acid is used with potassium chlorate, following exactly the conditions as laid down by Berthelot, the color of the graphitic oxide can vary from green to dark brown or yellow, and complete oxidation frequently requires six or eight successive treatments. Such is not the case when nitric acid is used which has been prepared from potassium nitrate that has been fused, and treated with large excess of boiling sulphuric acid. Under these

[1] Berthelot: "Recherches sur les états du carbone," *Ann. chim. phys.*, 4e série, 19, 392.

[2] This reaction also takes place at the ordinary temperature, but requires a very long time. When Ceylon graphite is introduced into a sealed tube, potassium chlorate and nitric acid (ordinary concentrated) added and allowed to stand at the ordinary laboratory temperature, there is obtained, after a year's time, a partial transformation into graphitic oxide.

conditions, on adding concentrated nitric acid to the dry graphite, then adding small quantities of potassium chlorate, the oxidation proceeds much more rapidly, and with natural graphite, it commences to appear at the end of the first treatment. It is necessary to use a greater weight of potassium chlorate than the graphite to be oxidized. The operation should be continued for twelve hours and should be finished at a temperature of 60°.

This temperature cannot be applied at the beginning of the operation, as the mixture of potassium chlorate, nitric acid, and carbon frequently explodes at 60°. The introduction of small quantities of organic material should also be avoided. At the end of the oxidations, the graphitic oxide is obtained in more or less well-defined crystals which have an oily appearance and are of a clear yellow color. In some cases the graphitic oxide is obtained nearly colorless. We also observed that when dry potassium chlorate is added to nitric acid which is highly concentrated, it immediately dissolves, giving an orange-red coloration, and under these conditions, at a temperature of 60°, whatever variety of graphite is used, after ten hours it is entirely transformed into graphitic oxide. The slightest trace of moisture retards the appearance of the red coloration and retards the speed of transformation. In the first work, I united the determination of the combustion point of graphite in oxygen with the determination of the densities of the principal varieties. The determination of the density is attended with much difficulty. It was impossible to deprive some samples of the gas which they mechanically retain, and as well their densities do not rise regularly with the rate of oxidation.

It must be remembered that certain natural varieties of graphite, when heated in presence of sulphuric acid or a mixture of potassium chlorate and sulphuric acid, take on the curious property of greatly increasing in size when heated to dull redness on platinum foil (Schafhaul, Marchand and Brodie). Luzi[1] has shown that it is only necessary to moisten these natural graphites with a small quantity of nitric acid (ordinary concentrated), in order to observe this increase of volume by heat, and the formation of little worm-like or dendritic products. Accordingly, from

[1] Luzi: "Sur le Graphite," *Ber. d. chem. Ges.*, **24**, 4085, and **25**, 214.

these properties, Luzi has divided the graphites into two classes; those which swell after treatment with nitric acid and which he gives the name of *graphites,* and those which under these conditions do not increase in size, he calls *graphitites.* The graphite of ordinary fusion and that produced by the action of the electric arc does not show this phenomenon after treatment with nitric acid.

We undertook the study of some natural graphites derived either from our earth or from meteorites. Subsequently, we prepared graphite by simple elevation of the temperature, and determined the properties of these different varieties. The numerous specimens of graphite were prepared by dissolving carbon in a large number of metals, and finally, we have been able to reproduce, at will, quantities of the swelling graphites that heretofore have not been prepared. These studies have enabled us to show how it is possible to convert, to a state of graphite, all the varieties of carbon—diamond or amorphous carbon.

A. Natural Graphites

Graphite from Ceylon.—This graphite has been studied by numerous investigators. Luzi has shown that it swells; it swells, however, much less than the graphite which we obtained from platinum fused in the electric furnace with excess of carbon.

Treated with potassium chlorate which has not been dried and commercial nitric acid, this variety of graphite gave, after seven successive treatments, a dark green, graphitic oxide and at the ninth treatment, a pale, yellow-colored oxide, the residue appearing as irregular fragments. This same graphite, when treated with dry potassium chlorate and concentrated nitric acid, gave graphitic oxide at the first treatment.

The details of the latter experiments are as follows:

First Treatment.—The graphite appeared dark green, with a golden reflection. Under the microscope, numerous particles of graphitic oxide could be seen.

Second Treatment.—Light green mass, appearing homogeneous. No graphite remained.

Third Treatment.—A yellow mass which still contained green particles.

Fourth Treatment.—The graphitic oxide was very pale yellow,

with a bright appearance. Under the microscope it appeared well crystallized (Fig. 8).

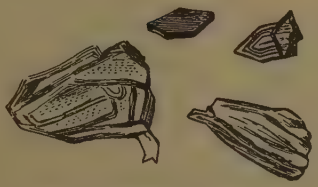

Fig. 8. Magnified 10 diameters.

Temperature of combustion of Ceylon graphite in oxygen, 665°; ash, 0.093; density, 2.23.

This graphite previously purified by fusion with potash and by hydrofluoric acid, could be completely transformed into graphitic oxide, and gave no residue of other varieties of carbon. This treatment was repeated on different samples and always gave the same result.

Graphite from Borowdale (Cumberland).—This graphite appears in compact fragments, having an amorphous structure with no cleavage. When treated with fuming nitric acid and heated on a piece of platinum foil, it did not swell; at the seventh treatment with the oxidizing mixture, it gave a pale yellow, non-crystalline oxide.[1] When this graphite was heated in a test-tube, it deflagrated, breaking up into small fragments. We thought that it contained gas, so we heated 1 cc. to dull redness in a vacuum The gas evolved was 4.1 cc. containing 0.7 cc. of air. The remainder (3.8 cc.) appeared, according to eudiometric analysis, to be a mixture of hydrogen and hydrocarbons. This occlusion of gas explains the explosive properties of Borowdale graphite under the action of heat. The graphite is impure; it contains 3.12 per cent. of ash. The latter preserved the exact form and volume of the graphite; it contains iron, alumina, manganese, lime, and silica. Iron and manganese predominate.

Graphite from Ticonderoga.—This graphite has been the subject of a detailed study by Luzi. It occurs in glistening, striated plates. Under the action of nitric acid it increased in volume very

[1] The treatment of the natural graphites was made with commercial nitric acid (68 per cent.) and with potassium chlorate which had not been dried.

distinctly and gave a leafy, crystalline mass; pressure caused it to again assume its original volume. Treated with the oxidizing mixture, it was completely transformed into a light green, graphitic oxide at the seventh treatment. The crystals preserved the original form of the graphite and on continuing the action of the oxidizing mixture, at the ninth treatment, took on a light yellow color. Examined under the microscope, the residue was seen to have lost its crystalline form.

Graphite from Greenville.—This graphite occurs in small crystals embedded in a calcareous gangue; under the microscope, the impression of the striations and equilateral triangles of the graphite could be seen on the rock. As Luzi has shown, it is a graphite which swells, and after eight successive treatments, can be transformed into yellow graphitic oxide.

Graphite from Omenask (Greenland).—This graphite is amorphous and very impure; the loss at red heat was 0.09 per cent., and it gives 21.04 per cent. of ash. The ash was nearly white; it contained a little silica and was very rich in alumina; it also contained lime and magnesia. Examined under the microscope this graphite appeared as very small crystals.

As has been shown by Luzi, this graphite does not swell.

Graphite from Mugrau (Bohemia).—Masses of graphite which do not show regular crystals when examined with a magnifying glass. They contain very small crystals, which are visible with the microscope when a high power is used. In appearance it resembles the graphite obtained by the action of a high temperature on amorphous carbon; it has certainly not been produced in a bath of liquid metal or fused substances. Loss at redness, 9.21 per cent.; ash, 37.32 per cent. The ash had an ochre color and contained a considerable quantity of silica, alumina, iron, and traces of manganese. This graphite did not swell. Its graphitic oxide, which is readily formed, is entirely amorphous.

Graphite from Scharzbach (Bohemia).—This graphite, which is soft, is similar in appearance to the graphite of Mugrau. Loss at redness, 6.82; ash, 44.27, contained silica, iron, alumina, lime, and manganese. The graphite did not swell, but gave a yellow amorphous graphitic oxide. It burns in oxygen at 620°.

Graphite from the South (Australia).—Very impure graphite,

when examined with a pocket lens showed no apparent crystallization. This graphite did not swell, but gave an amorphous graphitic oxide, yellow in color.

Graphite from Karsok (Greenland), brought back by Nordenskiöld.—Compact fragments with a leafy structure but without distinct crystallization. Ash, 17.9 per cent. The graphite did not swell but gave a green, amorphous graphitic oxide.

Graphites from the Blue Ground from the Cape.—We found in the blue ground of the Cape two graphites which had a very different appearance. The first occurred in regular crystals (*a*) and the second (*b*) in rounded leaves superimposed on one another, as represented in Fig. 9. This last specimen seems to

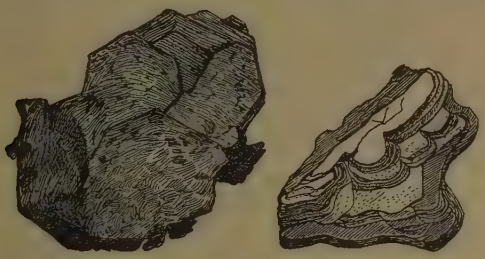

Fig. 9. Magnified 40 diameters.

have been formed under pressure. These graphites swell; the oxidizing mixture transforms them into graphitic oxide, opening them as the leaves of a book and preserving their form.

Graphite from Pegmatite.—A sample of graphite, which I studied, thanks to Damour, came from an American pegmatite (locality unknown). This pegmatite is very interesting. It is known that this eruptive rock has arrived at the surface of the earth after having been heated to a high temperature. In this specimen, the graphite appeared as finely crystallized plates, frequently more than 1 cm. in diameter completely diffused through the mass. It was easy to separate the graphite by repeatedly treating the rock on the water-bath with a large excess of 50 per cent. hydrofluoric acid. Both the feldspar and silica rapidly disappeared. The mass was treated with boiling water and dried on the stove. The pegmatite studied contained 12.77 per cent. graphite. The beautiful plates obtained were flexible, mirror-

like, and presented a surface on which the striations and the impressions of equilateral triangles were characteristic.

This graphite burned in oxygen at 690° ; it left a residue of 5.01 per cent. of ash, which consisted of silica, alumina and lime, and contained only a trace of iron. This latter metal was tested for, with potassium sulphocyanide and ferrocyanide; the ash was white and preserved the form of the crystals of the graphite. The temperature of combustion was higher than that of the graphite from Scharzbach or Ceylon. This graphite swells; moistened with concentrated nitric acid and heated to redness, it swelled greatly.

When this graphite was treated with the oxidizing mixture of potassium chlorate and nitric acid in large excess, it showed a very curious phenomenon. We introduced 6 grams of graphite in a 500 cc. flask, in the presence of 3 grams of potassium chlorate and about 20 cc. of nitric acid. At the beginning of the reaction, the graphite immediately assumed a beautiful green color, which showed that it was superficially attacked, and after several hours increased so much in volume that it half filled the flask. By a second treatment, it continued to swell, and the vessel had to be changed on account of the increase in volume. This was the only graphite which in the presence of nitric acid gave an increase of volume at 60°. After burning and destroying the graphitic oxide, no trace of black or transparent diamonds were found in the residue.

At the seventh treatment with the oxidizing mixture, complete transformation into graphitic oxide of a light green color was effected, and by a succeeding treatment, the graphitic oxide was completely decolorized. On examining under the microscope (using a low power) the fragments of quartz or feldspar on which the crystals of graphite rested, I was surprised to see that they showed the exact impressions of the surface of the crystals. These striations and triangles could not be removed by strong friction. This causes us to infer that the graphite pre-existed in the rocks, which, by their crystallization, have given rise to the pegmatite. By these characteristic properties, this graphite resembles, as we shall see later, the specimens which we obtained from the fusion of metals in our electric furnace, and that were

prepared under similar conditions. At the moment the pegmatite was formed, it was moulded by the crystals of quartz or feldspar, and left on the latter the impression of the details which are found on its surface.

Study of Some Meteorites.—The discovery of graphite in the meteorite of Canon Diablo caused me to study some of the metallic or holosidereal meteorites (Daubree) to ascertain if they all contained carbon and in what form they contained this element. It is known that among the meteorites which have been found on the surface of the earth, those which are entirely formed of iron-containing alloys are limited. However, they are so numerous that it has been posible to methodically study these holosidereal meteorites and ascertain the curious forms of the carbon they contain.[1]

It is impossible to ascertain in the depths of the earth, whether metals exist there and are the cause of the greater density, than that shown by the rocks at the surface; hence, we must content ourselves with the fragments which appear from the breaking-down of other planets. The number of specimens which we have been able to study has unfortunately been limited. We owe almost all to the kindness of Stanislas Meunier, who is still pursuing, with great earnestness, his work on these interesting problems.

No. 1. Iron from Kendall County, Texas.—Small sawed fragment, weighing 59.950 grams, having a smooth surface, showing rectangular figures. It contained some geodes which, examined with a pocket lens, appeared to be covered with a black substance. It was treated with hydrochloric acid diluted with an equal volume of water. The material was rapidly attacked, and there remained a crystalline metallic powder which quickly dissolved in aqua regia. After the treatment with aqua regia, the residue consisted of a black, amorphous material and a large quantity of small, irregular, transparent grains. Successive and repeated treatment with boiling sulphuric and hydrofluoric acids caused all the transparent portion to disappear. The black residue burned in oxygen, giving carbon dioxide. This was an amorphous carbon which was attacked with difficulty by the usual mixture of nitric acid and

[1] According to Stanislas Meunier, the number of iron meteorites which was known in 1880 was about 110 and more than half of these were found in the United States. "Meteorites," *Encyclopedie Chimique*, p. 439.

potassium chlorate. In this oxidation, no trace of graphitic oxide appeared. The transparent part was composed of sapphires and small, bottle-green grains that were rounded on the edges by the acids; they were not identified. They were completely destroyed by repeatedly fusing with acid potassium fluoride and treatment with boiling sulphuric acid.

The mass of iron from Kendall County contained amorphous carbon, but neither graphite nor diamond.

No. 2. Iron from Newstead in Roxburyshire, Scotland, Found in 1827. (Specimen in the British Museum).—The specimen weighed 8.10 grams, had a polished surface and showed a black color in parts. After treatment with hydrochloric acid, a large black residue remained, which was rich in carbon. Under the microscope it was not possible to recognize the brown filaments of carbon, but the presence of graphite could be readily distinguished. Three treatments with the oxidizing mixture gave a yellow graphitic oxide, distorted in shape and without a distinctly crystalline appearance. This compound burned by slight elevation of the temperature, with the formation of pyrographitic oxide. After destroying this graphitic oxide with boiling sulphuric acid, treating with acid potassium fluoride, then again with sulphuric acid, only a slight residue remained, which consisted of some transparent grains, with an attacked surface. After another treatment with acid potassium fluoride, then with boiling sulphuric acid, nothing could be detected with the microscope. The iron of Newstead in Roxburyshire contains amorphous carbon, graphite, but not the diamond.

No. 3. Déesite Discovered in 1866 in the Sierra de Deesa in Chili.—This meteorite, which was not homogeneous, gave, after treatment with hydrofluoric acid, considerable residue, which contained (1) irregular transparent grains; (2) rounded masses rich in silica; (3) a light black substance containing amorphous fragments having the appearance of graphite. We found no black filaments of carbon.

The black substance was entirely formed of graphitic carbon. In the first treatment with the oxidizing mixture, a green graphitic oxide was obtained, and on the third treatment elongated or distorted, transparent fragments remained. They took fire on heat-

ing, and were transformed into pyrographitic oxide. On subjecting the residue to the usual treatment with sulphuric acid, acid potassium fluoride, and finally with boiling sulphuric acid, only three small fragments remained, two of which were superficially attacked, and the third possessed great clearness. The latter was placed in a small platinum boat and heated to 1000° in a current of oxygen. On subsequently examining the boat under the microscope, using a low power, it appeared that this particle had lost its brightness, but did not burn in oxygen. This meteorite from Déesa did not contain the diamond, but contained a small quantity of graphite, and the form of graphitic oxide obtained indicated that this material had been submitted to pressure.

No. 4. Caillite, Iron from Toluca-Xiquipilso, Mexico (Fell in 1784).—This specimen, when dressed, showed a polished surface and weighed 69.050 grams. The residue obtained was very slight; examined under the microscope, it was composed of transparent grains, greenish fragments, small black grains, but contained no amorphous carbon and apparently no graphite. After treatment with acids, all the transparent fragments disappeared and after fusion with acid potassium fluoride, nothing remained.

Iron from Ovifack.—After the publication of our work on the blue ground of the Cape, and on the meteorites of Canon Diablo, Daubreé kindly placed at our disposal some samples of iron from Ovifack, discovered in Greenland by Nordenskiöld, in order to determine what variety of carbon they contained. We know, however, by a note appearing in the *Comptes rendus* that Nordenskiöld himself is occupied with this question. According to Daubreé[1] the pieces of iron are of at least three kinds: The first had a metallic appearance and was nearly black; the second had a light gray, metallic appearance and in the third the metallic substance instead of being continuous, appeared in globules or in grains, in a stone which was dark green and of the nature of a silicate. These three specimens were separately treated by following the method which we used to separate the microscopic diamonds from the blue ground of the Cape.[2]

[1] Daubreé: "Examen des roches avec fer natif, découvertes en 1870 par Nordenskjöld au Groënland," *Compt. rend.*, **74**, 1541 and **75**, 240.

[2] H. Moissan: "Sur la présence du graphite, du carbon et de diamants microscopiques dans la terre bleue du Cap," *Compt. rend.*, **116**, 292.

Sample No. 3: Thirty-four grams of the large pieces were dissolved in hydrochloric acid, and left a large residue. After treatment with boiling hydrofluoric acid, then with sulphuric acid, it decreased somewhat and under the microscope appeared to consist of:

(1) Perfectly spherical, dark green globules.

(2) Transparent, prismatic crystals with an elongated appearance.

(3) Fragments of blue and colorless sapphires, which could be separated with the pincers and distinctly recognized.

(4) A few fragments of amorphous carbon having an irregular form, a dull appearance, and a density below 2.

On repeating the alternate treatment with hydrofluoric and sulphuric acids, the size of the powder decreased. Several treatments with potassium chlorate and nitric acid caused the carbon to rapidly disappear. A final treatment by fusion with bisulphate, followed by washing with hydrofluoric acid, completely dissolved the residue.

Sample No. 2: Eighteen grams of this sample, treated with hydrochloric acid, gave a small quantity of a pulverulent substance and light carbon. Under the microscope there could be distinguished small particles of schreibersite, an opaque white substance in irregular masses, and a large number of refracting grains of all possible shapes.

The first treatment with hydrofluoric acid considerably diminished the size of the residue. After treatment with boiling sulphuric acid, the quantity of amorphous carbon increased, indicating the presence of a swelling carbon. The treatment with hydrofluoric and sulphuric acids was repeated. The residue was treated eleven times with the mixture of potassium chlorate and nitric acid (to form graphitic oxide) and was then fused with potassium bisulphate and was finally treated with hydrofluoric acid. Only some small, black, microscopic grains, superficially attacked, remained and disappeared by fusion with potassium bisulphate. Berthelot, in an investigation of a specimen of iron from Ovifack,[1] has already shown the existence of a similar substance which is not the diamond.

[1] Analysis quoted in the works of Daubreé.

Sample No. 1: Piece of 11 grams. After treating with hydrochloric acid, a small quantity of very light amorphous carbon remained. The first treatment with hydrofluoric acid decreased the residue, but with boiling sulphuric, the amorphous carbon increased. This sample contained swelling graphite. It also contained a non-swelling graphite, distinctly crystalline under the microscope, and which gave graphitic oxide by the action of chlorate. After fusion with bisulphate, no residue remained.

In the specimens of iron from Ovifack which Daubreé gave us, we have clearly detected the sapphire in one, amorphous carbon in all three; two of them contained swelling graphite; only one contained ordinary graphite, and in none were we able to find either black or transparent diamonds.

B. Artificial Graphites

Graphite Produced by Simple Elevation of Temperature.—We review in this chapter some graphites, which it is possible to prepare in the laboratory.

Diamond.—Jaquelin was the first to show that when diamond is heated in the electric arc, it is transformed into graphite. We would add to this observation the following facts: The graphite obtained shows an irregular crystalline form. The mixed crystals are thick and short, are glistening black, and show few facial planes. When formed by a current of 350 amperes at 70 volts, they are rapidly attacked by ordinary nitric acid and potassium chlorate. After three treatments, the transformation is complete and a graphitic oxide of a yellow color is formed. By combustion of this graphite we found it to contain 99.88 per cent. of carbon and 0.016 per cent. of ash.

Sugar Carbon.—Sugar carbon, purified by chlorine and placed in a closed crucible, was heated for ten minutes, with an arc of 350 amperes at 70 volts. The appearance of the carbon was essentially the same as before the operation, but it became grayer. None of the particles showed a crystalline appearance even when magnified. It left a gray mark on paper and by pressure took on the color of graphite. By treating three times with the oxidizing mixture it was converted into a pale yellow graphitic oxide. This graphite burned in oxygen at 660°. Its density was 2.19. On analysis, it gave: Carbon, 99.87; hydrogen, 0.032; and ash, 0.110.

Wood Charcoal.—Wood charcoal which had been previously purified was heated in a covered crucible. It was heated for ten minutes, five of which was with a current of 2200 amperes at 60 volts. The operation was discontinued on account of the projection of fused lime around the furnace. The wood charcoal preserved its original appearance, but, under the action of light rubbing, it took on a gray appearance and became bright. Under the microscope the wood fiber which had been slightly altered still preserved its form. This graphite was attacked with difficulty by the oxidizing mixture and gave a very pale yellow graphitic oxide, frequently forming a mass of small elongated rectangles or masses which still possessed a fibrous texture (Fig. 10).

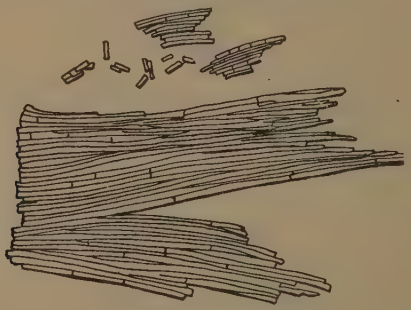

Fig. 10 Magnified 20 diameters.

Sublimed Carbon.—The sublimed carbon which condenses on the positive electrode of the arc, was not completely transformed by four treatments with ordinary fuming nitric acid and potassium chlorate. The graphitic oxide was at first greenish but finally became yellow. The fragments which were perfectly transparent, had the appearance of distorted leaves. Analysis gave the following figures: Carbon, 99.90; hydrogen, 0.031; ash, 0.017.

Carbon from the Extremities of the Electrodes.[1]—The extremities of the electrodes are transformed into a compact and soft graphite, without a trace of crystallization, taking on a dull gray when lightly rubbed and giving, on the third treatment with concentrated acid, a yellow graphitic oxide.

GRAPHITE PRODUCED FROM THE SOLUTION OF CARBON IN DIF-

[1] Fizeau and Foucault, Despretz, then Berthelot, have shown this formation of graphite under the action of the electric arc.

FERENT METALS.—These graphites can be produced by two different methods; either by displacing the combined carbon in a fused metal by another element or by utilizing the difference in solubility of carbon in the liquid metal at a very high and at a lower temperature.

The general procedure for obtaining graphite from the refractory metals, is to first prepare the carbide of the metal; then by another operation, this compound is saturated with carbon by means of the electric furnace. The fused mass, thus obtained, is treated with acids or heated to redness in a current of pure dry chlorine. The residue, made up of a mixture of amorphous carbon and graphites, is digested at 40° with fuming nitric acid, which destroys the first variety of carbon. The remaining graphite is treated with boiling hydrofluoric acid, then by luke warm sulphuric acid, and finally washed and dried.

Aluminum.—When aluminum is heated for five or six minutes in the electric furnace (350 amperes at 70 volts) in presence of sugar carbon, or simply in a carbon crucible, the metal forms the carbide, and on cooling, a mass is obtained which shows a yellow, crystalline fracture and contains aluminum carbide Al_4C_3. If the carbide is heated for ten or twelve minutes, it is partially volatilized, and there remains a gray material which is brittle, porous, and full of crystals of graphite. The latter were removed with hydrochloric acid, and purified by sulphuric and hydrofluoric acids. The graphite finally appeared as groups of small, glistening crystals, sometimes containing black filaments. Its density was 2.11. By the first treatment with the oxidizing mixture, the graphite swelled, and on the second, the smaller fragments were completely converted into graphitic oxide. Concentrated acid gave a pale green oxide with the first treatment, and became yellow with the second.

Silver.—This metal dissolves only very little carbon even at its boiling-point. The fusions of silver, slowly cooled in the electric furnace, are generally covered with a thin film. After dissolving the metal in nitric acid, bright plates of graphite were found in confused crystals. This graphite did not swell. Treated by the oxidizing mixture, it gave graphitic oxide at the first attack and with the sixth, the transformation was complete.

Manganese.—Manganese, prepared in the wind furnace, as Berthelot has shown, contains only amorphous carbon; but when the carbide is heated four or five minutes, in presence of an excess of carbon, by an arc of 350 amperes at 50 volts, the ingot, which is formed, contains crystals of graphite and is covered with them.[1] This graphite forms large, bright plates which appear in beautiful, regular hexagons. Treated with the oxidizing mixture, it gave, on the third treatment, a complete transformation into a yellow graphitic oxide which was well crystallized.

Nickel.—Nickel, heated in the electric furnace, gives a graphite, which, by its appearance and form, recalls gray cast iron, but the crystals are more distinct. It is readily transformed into graphitic oxide at the second treatment.

Chromium.—The carbides of chromium that we shall describe later, readily dissolve carbon. On cooling, a metallic ingot is formed, which, after treatment with acid, gives crystals of graphite which are much smaller than those obtained from manganese. The crystals are irregular, less bright, and are more difficultly attacked than the graphites obtained from iron and manganese, which have a higher fusing point than chromium. With the oxidizing mixture, they are apparently not converted until the third treatment. They give a voluminous light yellow graphitic oxide which forms irregular masses (Fig. 11).

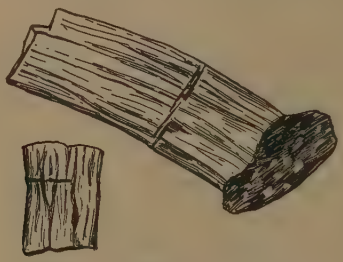

Fig. 11. Magnified 40 diameters.

Tungsten.—The melting-point of tungsten is higher than that

[1] This experiment seems to be a contradiction of the fact which I have previously shown of the ready volatilization of manganese in the electric furnace. It indicates that metallic manganese is much more volatile than manganese carbide. The latter substance, however, finally disappears also under the continued action of the heat of the electric arc. Jordan has called the attention of metallurgists to the ready volatilization of manganese in the blast-furnace.

of chromium; its graphite forms small, bright, black crystals which have a regular form. The conversion into graphitic oxide scarcely began at the third treatment.

Molybdenum.—The graphite of molybdenum appears as a mass of small, bright, black crystals. Sometimes these crystals form a regular felt, or are united into round masses. It is more difficultly attacked by the oxidizing mixture than the preceding. The graphitic oxide obtained was yellow and had a more or less regular form.

Uranium.—Masses of small, bright, black crystals, difficultly attacked by the oxidizing mixture. The graphite from uranium gave a yellow graphitic oxide of irregular form.

Zirconium.—The graphite from this metal appears as a felting of small, tangled masses, with a perforated surface, frequently terminated by longer or shorter filaments (Fig. 12). It was attacked slowly and with difficulty by the oxidizing mixture and gave a yellow graphitic oxide (Fig. 13).

Fig. 12. Modified 40 diameters.

Fig. 13. Modified 40 diameters.

Vanadium.—Of all the refractory metals that I have been able to prepare in the electric furnace, vanadium is the most infusible. Its graphite is rarely crystalline; it generally occurs in very fine, irregular fragments which are perforated or slightly hollowed and sometimes show rounded extremities.

Titanium.—Titanium carbide, TiC, whose preparation we have shown, readily dissolves carbon and, on cooling, allows it to separate in the form of a graphite. This latter body, which swells slightly, occurs in crystals or rounded masses similar to the graphite obtained from vanadium. Its graphitic oxide, which at

the beginning of the treatment is chesnut-brown, rapidly becomes pale yellow.

Silicon.—When silicon is heated in the wind furnace, it dissolves carbon which subsequently separates as graphite spangles having a bright, black and well-crystallized appearance, and forming a yellow graphitic oxide.

At the temperature of the electric furnace, silicon does not give graphite, but forms crystalline silicon carbide. On the fourth treatment with the oxidizing mixture, the fragments of graphite scarcely commence to be converted into graphitic oxide. On continuing the action of the chlorate and the acid, a yellow graphitic oxide is obtained which preserves the form of the original fragments.

Thus artificial graphite can be obtained either amorphous or crystalline. Its density varies between 2.10 and 2.25. Its temperature of combustion in oxygen is in the neighborhood of 660°. Many varieties of graphite exist, as well as many varieties of amorphous carbon. The stability of graphite is increased with the temperature to which it has been carried. This is evident from the greater or less resistance it offers on conversion into graphitic oxide. Moreover, in proportion as the fusing point of the metal in which the graphite is formed, is raised, so is the resistance to oxidation increased. The influence of temperature on the stability of graphite can be shown very simply. The natural graphite of Ceylon is transformed into graphitic oxide by a single treatment with the well-dried, oxidizing mixture. If this graphite is heated for ten minutes in the electric furnace with a current of 1200 amperes at 70 volts, the yellow graphitic oxide can be scarcely seen after three treatments. A simple elevation of the temperature thus renders the graphite harder to attack.

Displacement of Carbon by Boron and Silicon in Melted Cast Iron.—The investigation of the solubility of carbon in different metals at increasing temperatures, led us to study the action of boron and silicon on liquid iron carbide. The action of boron on iron has not yet been studied,[1] or else, in the work attempted in this direction, the boron was not detected, after the

[1] This has been particularly due to the fact that no method was known for the preparation of pure boron. We have given this preparation in 1892. *Compt. rend.*, 114, 392.

reaction, in the metal which had been submitted to its action. As regards the action of silicon, no work has been done in a systematic manner. It has been known for a long time, in the iron industry, that cast irons which are low in carbon are rich in silicon; but the action of silicon has not been accurately determined. Melted iron is a liquid in which, as we shall show, the reactions are frequently as clear as in the aqueous solutions which we handle in the laboratory at ordinary temperatures. The complexity of certain irons, which often contain as impurities a large number of compounds, only render the reaction more obscure.

Action of Boron on Gray Cast Iron.—We began with a gray iron from Saint-Chamond, which contained 3.18 per cent. of total carbon and 0.5 per cent. slag.[1]

Ten grams of this iron were placed in a porcelain boat lined with 2.3 grams of boron. The whole was strongly heated in a combustion furnace in a porcelain tube in a current of dry hydrogen. At the end of the experiment a well-fused mass was found which was covered with a black layer of graphite. The metal had a yellow color and showed on its surface some long, crystalline prisms. These contained, on analysis, 8 to 9 per cent. boron. It was boron containing cast iron mixed with partially crystallized iron boride. This boron containing regulus, contained only 0.27 per cent. carbon and gave no slag when the residue was burned in oxygen. Boron readily combines with the impurities in the iron and these went into the slag. It acted on iron oxide, which was dissolved in the metal in a manner similar to that which Troost and Hautefeuille have ascribed to manganese.[2]

We therefore conclude from this reaction that the boron has driven out the carbon in the ratio of 1 : 10 and at the same time has eliminated the material which forms the slag. This experiment was repeated four times on another sample of gray iron from Saint-Chamond which contained 3.24 per cent. of carbon and 0.418 per cent. of slag. After the action of the boron, the following figures were obtained:

[1] In the analysis of the cast irons, the mixture of the different varieties of carbon was separated by chlorine or mercury bichloride. The residue was burned in oxygen and the ash which remained is called the slag.

[2] Troost et Hautefeuille : " Étude calorimétrique sur les carbures, les siliciures et les borures de fer et de mangànese," *Ann. chim. phys.*, 5e série, 9, —.

	(I)	(II)	(III)	(IV)
Carbon	0.56	0.28	0.17	0.14
Slag	0.02	0.00	0.03	0.01

We substituted for the gray iron, a white refining iron from the blast-furnace of Saint-Louis, in Marseilles. This iron contained 3.85 per cent. of carbon and 0.36 per cent. of slag. After the action of the boron, it contained only 0.24 per cent. of carbon and 0.06 per cent. of slag. We varied the form of the experiment and did not allow a great excess of boron to act on the fused iron. 500 grams of gray iron from Saint-Chamond were fused in a wind furnace and when the iron was perfectly fluid, 50 grams of an iron which contained 10 per cent. of boron were added. After shaking, the crucible was covered and allowed to cool. When the boron containing iron was added to the gray iron, it floated on the metallic bath and only dissolved by agitation. On cooling, the regulus had a leafy appearance possessing great hardness; it could not be scratched with an engraving tool, and had the appearance of white iron. By the action of boron the carbon content of this iron decreased from 3.75 to 2.83. Boron thus displaces the carbon, of which a portion appears as graphite between the metallic mass and the crucible.

Displacement of Carbon by Silicon. We repeated the same experiment, heating some pieces of gray cast iron in a boat lined with powdered crystalline silicon. Silicon, under these conditions, displaces the carbon, which is found as graphite on the top of the metal. But, as we have already remarked, white or gray iron made in the blast-furnace is a somewhat complex combination. The experiment was repeated under simpler conditions. An iron rich in carbon was first prepared in the electric furnace, from wrought iron and sugar carbon, and to the fused mass some fused silicon was added. On cooling, the mass had a smooth upper surface, had the appearance of silicon containing cast iron, a bright white fracture, and contained only a trace of combined carbon and no graphite. But in the center of the mass there was a large cavity which nearly divided it into two parts. This cavity was filled with quite a quantity of bright and well-formed crystals of graphite.

Boron and silicon evidently displace carbon in iron or in iron

carbide.[1] These bodies, when maintained at a sufficient temperature, behave exactly as the aqueous solutions of certain compounds, in which we precipitate or displace substances in solution or in combination. If the displacement of the carbon is not entirely complete, a state of equilibrium is established between the silicide and carbide of iron, an equilibrium in which the conditions vary with the temperature and with the impurities which are contained in the bath. This is generally the case with white or gray cast irons. This work led us to study the graphites in iron.

Graphites of Iron.—Thus far, we studied the graphites obtained either by simple elevation of the temperature on various kinds of carbon, or by the solution of carbon in the difficultly fusible metals. We thought that it would be well to add to this first work, the study of the different varieties of carbon produced by the same method under different conditions of temperature and pressure. From this point of view, the most important metal from its application being iron, we directed our attention to it.

The melting-point of gray cast iron being in the neighborhood of 1150°, the graphite that we studied, which came from the gray cast iron from Saint-Chamond, was therefore formed somewhere near this temperature. The mixture of amorphous carbon and graphite which remains when this cast iron is treated at a low red heat with chlorine, was repeatedly treated with fuming nitric acid, then with hydrofluoric acid. The graphite which remained, after washing and drying, possessed the following properties: Its density was 2.17; it burned in oxygen at 670°; it appeared in groups of very small crystals, which showed distinct hexagonal terminations and in bright, irregular masses with good cleavage (Fig. 14). The color is inclined to the gray. Treated with the ordi-

Fig. 14. Magnified 20 diameters.

nary concentrated nitric acid and potassium chlorate it was at-

[1] The temperature at which all of these operations were made was not sufficiently high for the formation of appreciable quantities of the borides or silicides.

tacked on the second treatment, and on the third treatment was completely converted into a green graphitic oxide which was fairly well crystallized. If, as we have previously shown, concentrated nitric acid had been used and if moisture had been avoided on the first treatment a light green graphitic oxide would be formed, becoming yellow on the second.

In another series of experiments, we separated the carbon by treating the same iron with a mixture of hydrochloric acid, to which a small quantity of nitric acid had been added. The addition of the latter oxidized the iron to ferric chloride which is soluble in dilute acids. This treatment also destroyed a large part of the amorphous carbon. The residue was washed and dried, and repeatedly treated with fuming nitric acid. In order to free this graphite from the mineral substances which it still contained it was first treated with hydrofluoric acid, then boiling sulphuric acid. Under these conditions there remained a substance which in appearance resembled graphite but contained only 80 to 85 per cent. carbon, 1.30 per cent. ash, and 0.15 per cent. hydrogen. The content of hydrogen varied between 0.15 and 0.80 per cent.[1] As this graphite was kept at a dull red heat during the analysis I am led to believe that during the treatment with acid a complex body was formed containing carbon, hydrogen, oxygen, and nitrogen, and stable enough to resist the temperature of 400°.

The formation of these compounds seems worthy of note in the study of the graphites of the metals when these graphites have not been prepared at a high temperature. These compounds appear to be formed by the addition of hydrogen, rather than by the oxidation of iron carbide. They can be classed with the compounds obtained by Eggertz in the action of iodine water on iron and by Schützenberger and Bourgeois on treating a white iron with a solution of copper sulphate.[2]

Graphite from Strongly Heated Cast Iron.—A very good quality of wrought iron was introduced into a crucible of sugar carbon, and the crucible and contents submitted, in the electric furnace, to the action of an arc of 2000 amperes at 60 volts. The

[1] This graphite contained nitrogen, which appeared as ammonia when treated with soda-lime, and which appeared as red vapors when the graphite was burned in oxygen.

[2] Schützenberger and Bourgeois : "Recherches sur le carbone de la fonte blanche," *Compt. rend.*, 80, 911.

experiment lasted ten minutes. Under these conditions, the iron dissolved somewhat large quantities of carbon and became viscous. We were surprised to find that at this high temperature, the crucible could be inverted without the metal running out. On allowing the mass to cool, protected from the air, a brittle mass formed on the bottom of the crucible which was covered with beautiful crystals of graphite, frequently several millimeters in diameter. On the surface of the metal, some fragments were found which contained very little iron and which were formed by a mass of graphite crystals. At this high temperature a portion of the metal had been volatilized.

The ingot was subsequently treated with chlorine at a low red heat and the residue treated with warm, fuming nitric acid to destroy any amorphous carbon. This graphite appeared in large, bright, crystals which had a beautiful black color, and were frequently very regular. A group of very small crystals were also found which formed a kind of felting apparently resulting from the condensation of the vapor of carbon. This graphite had a density of 2.18; it burned in oxygen at about 650°; it contained 99.15 per cent. of carbon and only 0.17 per cent. of ash and 0.28 per cent. of hydrogen. It was much finer than the graphite from ordinary cast iron, and apparently contained only a small quantity of the complex hydrogen compounds which are always found in the graphite of ordinary cast iron which has been treated with dilute acids. This graphite having been heated to a high temperature, showed great stability when treated with the oxidizing mixture. The first and second treatment was without effect; only at the third, the formation of a light-colored graphitic oxide began and this had the appearance of smoked glass. The graphitic oxide appeared in regular hexagons. With concentrated acid the treatment had to be repeated four times in order to effect complete transformation into yellow graphitic oxide (Fig. 15). These two experiments clearly demonstrate that the resistance of iron graphite to oxidizing agents is a function of the temperature to which it has beeen raised.

Graphite from Cast Iron Cooled in Water.—In order to introduce pressure in the preparation of graphite, we used a method which served to strongly compress the carbon in the liquid iron;

we suddenly cooled the melted iron with cold water. After treatment with chlorine, similar to that previously described, there re-

Fig. 15. Magnified 20 diameters.

mained a bright residue having a beautiful black color and which was entirely different in appearance from all of the other graphites. It consisted of short, thick crystals, whose angles were frequently blunted and of irregular masses whose rounded form indicated the commencement of fusion (Fig. 16). In appearance,

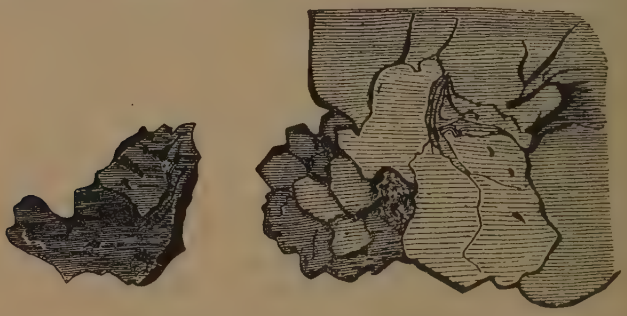

Fig. 16. Magnified 30 diameters

it reminds one of sample *b* of graphite from the blue ground. Its density was 2.16; it burned in oxygen at 660° and on analysis gave the following results: Ash, 1.29; hydrogen, 0.64. Treated with the ordinary oxidizing mixture, it began to be transformed into graphitic oxide only at the third treatment. With concentrated nitric acid, it required four treatments to form a crystalline graphitic oxide.

Graphite Produced by the Action of Silicon on Cast Iron.—In the preceding experiments, attention was directed only to the preparation of graphite by the solution of carbon in iron. I also

desired to study the carbon prepared by a chemical reaction and to this end threw out the combined carbon in cast iron by means of silicon, using the reaction which we previously studied. We will not repeat the details. The graphite obtained

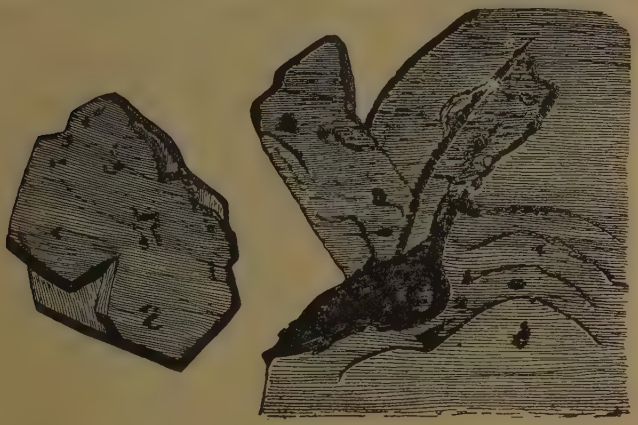

Fig. 17. Magnified 20 diameters.

by this means had a beautiful black color and frequently crystallized very regularly (Fig. 17). Its density was 2.20. On analysis

Fig. 18. Magnified 20 diameters.

it gave: Carbon, 98.82; ash, 0.85; hydrogen, 0.20. It was readily destroyed by the oxidizing mixture and on the first treat-

ment with ordinary nitric acid and potassium chlorate, some fragments of graphitic oxide could be seen which had begun to form on the edges (Fig. 18). The transformation was complete on the third treatment; the greenish yellow graphitic oxide became clear and bright and the crystals in a remarkable manner preserved the original appearance of the graphite.

With concentrated nitric acid, the transformation into yellow, crystalline graphitic oxide was complete with the third treatment.

Presence of Hydrogen in the Different Graphites.—All the graphites that we studied contained hydrogen. This hydrogen can arise, either by a physical phenomenon as the condensation of hydrogen gas in the graphite[1] or by a chemical phenomenon such as the taking up of hydrogen by iron carbide or of certain varieties of amorphous carbon which are contained in the iron. To show that this hydrogen is not in combination in the graphite we made the following experiment: An ingot of iron saturated with carbon, under the action of an arc of 2,200 amperes at 60 volts, was allowed to cool in a closed electric furnace. On cooling, the metallic ingot became covered with a considerable quantity of graphite. This graphite was collected, without being separated from the small particles of iron which it contained, without being treated by a reagent, and a small quantity was placed in a boat and heated for ten hours in vacuum to a temperature of 500°.

When the apparatus was still at 200°, dry air was allowed to enter, then it was weighed in a glazed tube and finally placed in the boat, still hot, in a combustion furnace, and served as a blank. Under these conditions the combustion of 0.076 gram graphite in oxygen gave an increase in weight of 1 mg. of water, corresponding to only 0.014 gram of hydrogen, a quantity within the limit of error of the experiment. When the conditions of formation of graphite in the same metal, iron, were studied, by varying the temperature and pressure, the following results were obtained:

(1) Under ordinary pressure, the purest graphite is formed at the highest temperature.

(2) Graphite which has been obtained at a high temperature is more stable in presence of nitric acid and potassium chlorate.

[1] Cailletet showed long ago by his delicate experiments that fused cast iron dissolves considerable hydrogen gas.

(3) Under the influence of pressure, the crystals and the masses of graphite assume the appearance of a fused substance.

(4) The small quantity of hydrogen, which is invariably contained in graphite, diminishes as the purity increases. Graphite treated with no reagent and only previously heated in a vacuum gives no water when burned in oxygen.

(5) In the treatment of cast iron by acids, hydrogen and oxygen compounds appear; they resist the temperature of a low red heat, and, like graphite, are destroyed by burning.

C. Graphite which Swells

In the blue ground from the Cape of Good Hope we found a variety of this graphite which is similar to the graphites, described by Luzi in New York state (Ticonderoga), in Ceylon, Quebec, Spain and in Norway.

Our studies, on these different varieties of carbon, have brought about the preparation at will of this particular species of graphite which is abundantly distributed in nature, but which had not been prepared in the laboratory. To obtain this graphite which swells, it is only necessary to quickly cool melted iron in water. On the surface of the iron ordinary graphite is found, and a little below the surface there is found a quantity of graphite which, when treated with nitric acid, rapidly swells. A mixture of the two graphites can thus be prepared, or as Luzi designates them, a mixture of graphitite and graphite. When only the swelling graphite is desired it is preferable to use some other metal than iron, to dissolve the carbon. The metal which gives the best results is platinum.

Graphite which Swells, from Platinum.—About 400 grams of platinum were fused in a carbon crucible in the electric furnace, using a current of 450 amperes at 60 volts. The platinum melted rapidly and after a few minutes, distilled and condensed in the form of melted drops on the cooler parts of the electrodes. The liquid platinum in a short time became saturated with carbon at this high temperature. After six or eight minutes the current was interrupted and the metal allowed to slowly cool in the crucible. Under these conditions, a solution of carbon in platinum was formed and the excess of carbon crystallized in the mass as graphite. The metallic mass was heated with aqua regia, after

which the residue was washed with boiling water and dried. The yield was 1.45 per cent.

Properties.—This graphite was of a slate-gray color, somewhat lighter than that from cast iron. It appeared in individual hexagons, but more frequently as superimposed crystals. Under the microscope, the hexagonal plates, which were strongly reflecting, showed parallel striations and sometimes the triangular impressions which were not as strong as those on the diamond. Some reflecting surfaces also showed parallel lines of various forms.

The density of this graphite varied between 2.06 and 2.18; it burned in a current of oxygen at 575°. This graphite, when submitted to the action of nitric acid in the treatment with aqua regia, swelled greatly as soon as it was heated to dull redness. Indeed, at 400°, it acted similar to mercury sulphocyanide. The light mass, obtained under these circumstances, was formed of graphite, for, when acted on with the mixture of potassium chlorate and nitric acid, at the first treatment, there was formed a green-colored graphitic oxide which became light yellow on the second treatment. Potassium nitrate, at the melting-point, was without action on this variety of carbon. When heated a little higher, the graphite began to swell and was fairly rapidly destroyed, but generally without taking fire. Fused chromic acid did not readily attack it. However, when this oxidant commenced to evolve oxygen by elevating the temperature, a small quantity of carbon dioxide was evolved. On the contrary, gently warmed iodic acid readily attacked it with the evolution of carbon dioxide and iodine vapor. Heated sulphuric acid did not alter it in appearance and the boiling acid did not give sulphur dioxide. Fusion with sodium carbonate rapidly destroyed it.

The analysis of this swelling graphite was made by combustion in a current of pure oxygen, and weighing the carbon dioxide which was formed. The following figures were obtained:

	I.	II.
Carbon	99.02	98.84
Ash	1.10	1.02

As the increase in weight of the tube for the collection of water was only 1.5 milligrams we concluded that this graphite either contained no hydrogen or only an insignificant quantity. The ash, when

examined with the microscope, presented the appearance of spongy platinum, and by treating with aqua regia it was possible to recognize this metal.

Cause of the Swelling.—There yet remained to be determined what causes the swelling of this variety of carbon. On this point we give the following experiment: About 1 cc. of this graphite was heated in a glass tube in a current of air free from carbon dioxide. As soon as the temperature approached a low red heat, the mass rapidly swelled and at the same time evolved nitrous fumes and a small quantity of carbon dioxide which was collected in baryta water. A last addition of acid gave no precipitate in the baryta water. It, therefore, appears that the property of swelling can be attributed to a sudden evolution of gas, perhaps by the action of the heat on a small quantity of amorphous carbon under pressure between the hexagonal plates of the graphite, or by the decomposition by heat of a small quantity of graphitic oxide which is produced by the action of the nitric acid on a trace of amorphous graphite mixed with the crystallized graphite, and which is more readily attacked. At all events, it is the sudden evolution of a small quantity of gas which has been expanded by heat, that produced this particular swelling.

Graphite which Swells from Different Metals.—On continuing this work, we observed that many other metals can replace platinum in the preparation of this variety of graphite. In all of our work on the different varieties of graphite, we found the curious fact that of all the graphites obtained by the simple action of a high temperature on any variety of carbon (diamond, lampblack) or by the condensation of the vapor of carbon, none showed a trace of increase of volume by the action of concentrated nitric acid. On the contrary, all of the graphites prepared at a high temperature, by solution of carbon in a fused metal, were of the swelling variety.

Zirconium, vanadium, molybdenum, tungsten, uranium, and chromium gave graphite which swelled. This was also true of aluminum, which is only saturated with carbon at a high temperature. This phenomenon of swelling, under the action of nitric acid, not only shows the action of the metal on the carbon, but particularly the temperature at which the graphite is formed. In

fact, a gray iron from Saint-Chamond gave, after treatment with chlorine and destruction of the amorphous carbon with nitric acid, a graphite which did not swell at all in presence of nitric acid with an increase of temperature. This same iron, strongly heated in the electric furnace, under the action of an arc of 2000 amperes at 50 volts, gave, on cooling, a graphite which swelled greatly.[1] I remember that this swelling was produced by the action of ordinary nitric acid. It is possible to dry the graphite, which has been moistened with the acid, in an air-bath at 120° for an entire day, and as soon as the temperature is raised, the mass greatly increases on heating.

In all of these varieties of graphite, produced by the action of an intense heat, the temperature of swelling is not very high. It varies between 165° and 175°. Hence it is not necessary to heat this graphite as high as dull redness. We introduced into a glass tube a small quantity of this swelling graphite which had been previously treated with nitric acid, then dried in an air-bath. After exhausting the air from the tube, it was sealed off with a burner. The swelling was produced in the vacuum at the same temperature as before, and there was evolved a gaseous mixture, containing carbon dioxide, nitrogen, and red vapors, while small drops of nitric acid condensed on the sides of the tube. Thus, as we have remarked, this swelling can be ascribed to the sudden evolution of a volume of gas, expanded by the heat. These experiments show that the swelling graphites, prepared in the laboratory, can be as plentiful as those which are found in nature. Without doubt they explain the formation of the natural swelling graphites, some of which give, as is known, an ash that is frequently rich in iron oxide. These graphites appear to have been produced at a high temperature, without great pressure, in the midst of masses of iron which afterwards have disappeared under the action of such gases as hydrochloric acid.[2]

Graphite is a body which resists most of the chemical agents. At dull redness, water vapor and air are without action on it. It

[1] In the study which we have made on the diamond ground from the Cape mines, we found that the serpentine breccia contained a greater quantity of crystalline swelling graphite than diamonds. The ash of this graphite was very ferruginous.

[2] This formation of readily volatile iron chloride is possibly the cause of the distribution of iron during the first geological periods.

is consequently found separated from its metallic gangue, and forms larger or smaller masses where it has been disseminated in the rocks.

Conclusions.—According to the definition of Berthelot, we give the name of graphite to the varieties of carbon generally crystalline, having a density of about 2.2 and which, on treatment with an oxidizing mixture of potassium chlorate and nitric acid, give graphitic oxide which is easy to recognize. These graphites are found on the surface of the earth and in some meteorites. They can be divided, according to Luzi, into graphites which swell and graphites which do not swell, when gently heated in presence of a trace of nitric acid. We found, in an American pegmatite, a highly swelling graphite. The iron of Ovifack, and the blue ground of the cape also gave swelling graphites. Some of these graphites, as those from Borowdale, are full of gas, which they retain with great energy. The graphites obtained by mere elevation of the temperature in the electric furnace, do not swell at all.

On the contrary, all those which were obtained from a fused metal at a high temperature, either by difference of solubility or by chemical action, have the property of swelling readily. This swelling graphite is readily prepared in the electric furnace by allowing platinum to boil in a carbon crucible. The swelling of this variety of carbon is explained by the sudden evolution of gas. Artificial graphites can be either amorphous or crystalline. Their density varies between 2 and 2.25. Their temperature of combustion in oxygen is in the neighborhood of 660°. When pure, they do not contain hydrogen. A graphite obtained in the electric furnace, which was not treated with a reagent, and which was previously heated in vacuum, gave no water when burned in oxygen. On the contrary, ordinary cast iron, treated with dilute acids, gives hydrogen and oxygen compounds, which are not destroyed at a low red heat.

When graphite is prepared in the electric furnace, its resistance to oxidation is proportional to the temperature to which it has been raised. An easily attacked graphite, such as the graphite from Ceylon, can be rendered difficult to attack by strongly heating. This explains the existence of the many varieties of graphite analogous to the different varieties of amorphous carbon.

THIRD PART

Preparation of the Artificial Diamond

General Remarks.—When Lavoisier demonstrated in his memorable work that diamond was crystalline carbon, attempts at its artificial preparation were soon made. The attempts made in this direction are numerous, but little has been done in a methodical and systematic manner. If we except some important works, we see from the historical part of the question, how much of contradictory or doubtful matter has been published. Moreover, while the number of experiments has been large, the publications have not been as extended as one would at first expect. It appears, without doubt, that many of the workers have considered more the artificial preparation of the diamond than the study of the different allotropic forms of carbon. Considered from this point of view, the question was incomplete. On account of these views, we desired to study in as general a manner as possible the three varieties of carbon: Amorphous carbon, graphite, and diamond.

In the preceding chapters we have given the results obtained with the amorphous carbons and the graphites. In this we take up that which relates to the diamond. At the beginning of our work, we were convinced that it is possible to prepare artificial diamonds; the first crystals obtained were microscopic. When the size of the quartz crystals which are found in nature is compared with the synthetic crystals obtained by the method of Daubreé, we should not expect to prepare, in the beginning of a study on crystallized carbon, diamonds of many carats.

We call attention to the many researches and successive efforts made to effect the synthesis of rubies of any size, and having the coloration and brilliancy which we find in some rare specimens of this beautiful gem. We therefore pursued the work by studying carefully, always with the microscope, the residues, frequently very small, obtained in our experiments after the various chemical actions of which we shall speak later. It is due to the microscope that we have been able to carry out this work.

Finally, it is necessary to separate a powder of crystalline car-

bon not only from a large excess of amorphous carbon and graphite, but also from silica, the silicates, crystalline or fused alumina; in a word, all the substances that inorganic chemistry can furnish. Here the important work of Berthelot[1] serves as a guide and model. The diamond can be defined as follows: A simple body, having the greatest hardness, a specific gravity of 3.5, burning in oxygen above 700° and of which 1 gram by its combustion in oxygen, gives 3.666 grams of carbon dioxide.

The three important factors are: The hardness, density, and combustion in oxygen. Heretofore the ordinary clear diamond scratched all other bodies and was scratched by none. We have demonstrated that this great hardness, which was believed to be a peculiar characteristic of the diamond, is also found in some of the new compounds that we have prepared in our electric furnace. The carbon boride slowly cuts the diamond and the titanium silico-carbide has a hardness which is almost equal to that of the diamond. On the contrary, certain varieties of *bort* of indistinct crystallization well known to jewelers, and the black diamond always deserving the name *αδα μα*, possess greater hardness than the new compounds.

The electric furnace has increased the number of bodies which are hard enough to scratch the ruby. Among these may be mentioned silicon carbide, and many carbides, borides, nitrides, silicides, and silico-carbides of the metals.

It appears, in this brief résumé, that a number of bodies can scratch the hardest corundum without being diamond. The peculiarity of scratching ruby is, consequently, not a fact of the greatest value. Neither can the great density of crystalline carbon (3.5) serve to distinguish only the diamond. Certain titanium compounds, the carbo-silicides, carbo-borides of complex formula of the metals, can have equal or greater densities than crystalline carbon.

The combustion at red heat with formation of carbon dioxide is not sufficiently characteristic. Carbon boride and some metallic boro-carbides, very hard and very dense, can partially burn at redness with the formation of carbon dioxide. The combustion in oxygen has only definite weight when a quantity of carbon dioxide

1 Berthelot: "Sur les différents états du carbone," *Ann. chim. phys.*, 4e série, 19,392.

is formed which, when weighed, corresponds to the atomic weight of carbon. It is necessary then in order to be considered diamond, that it must possess the three properties: Hardness, density, and the property of burning in oxygen, forming 3.666 grams carbon dioxide for one gram of substance burned. Each experiment, which rests on but one of these three properties, is insufficient and can lead to a false conclusion. Before describing my work on the production of artificial diamonds, I wish to thank my assistant, Lebeau, who in all this work has given the most devoted and assiduous help.

HISTORICAL.—In this part we will not review the complete history of the work on the preparation of artificial diamond; this would lead us too far. We will give only a short description of the most important work published in this direction.

In 1828, J. N. Gannal presented to the Académie des Sciences a paper entitled "Observations faites sur l'action du phosphore mis en contact avec le carbure de soufre pur." In this work, Gannal announced that on allowing a solution of phosphorus in carbon bisulphide to remain for three months under a layer of water, there was formed crystalline carbon, some parts of which were of the size of a grain of millet. We repeated the work of Gannal, according to his description, and were never able to obtain anything but some small fragments of glass or small grains of silica which were completely soluble in hydrofluoric acid.

Later we varied the experiments by lengthening the time. At the end of six months, a year, and five years we obtained nothing at all. The phosphorus was replaced by antimony under similar conditions and the result was always negative. We never obtained crystals which were visible to the naked eye, and the microscopic particles, which were separated by treating with carbon bisulphide, and then with distilled water, always disappeared in boiling hydrofluoric acid. Gore also repeated the work, obtaining no better results.

We need only mention the work of Cagniard-Latour.

Incidental to his work on the volatilizaton of refractory bodies by means of the electric arc[1] Despretz endeavored to prepare arti-

[1] Despretz: "Fusion et volatilisation de quelques corps réfractaires sous la triple action de la pile voltaïque, du soleil et du chalumeau." *Comptes rendus* de l'Académie des Sciences, 1849, **28**, 755, and **29**, 48, 545, and 709.

ficial diamond. The work of Despretz has been thoroughly discussed. It is known that this worker , on allowing an electric arc to play between a carbon electrode and a bundle of platinum wires, obtained a crystalline powder that scratched ruby, and this property only was brought out as a proof that the substance was crystalline carbon. Many chemists have doubted the results of this experiment. It is, however, very probable. The small, bright particles, obtained by Despretz, were silicon carbide or possibly boron carbide, whose hardness is great enough to easily scratch the ruby and as well, soft diamond.

The action of the electric arc on carbon has never given crystalline carbon. In the work of which we shall speak later, Berthelot studied the extremities of the electrodes of the arc light which were used for some time, and after destroying the graphite, could not find a trace of diamond. We would also add that the small carbon capsules and the electrodes of Despretz, which were deposited at the University of Paris, were examined in 1870 by Berthelot. These capsules and the extremities of the electrodes were completley transformed into graphite, as Despretz had said, but only into graphite, as Berthelot showed by the transformation of this variety of carbon into graphitic oxide.

In 1866, as a result of a geological theory of de Chancourtois, Lionnet presented to the Académie des Sciences a paper, "Sur la production naturelle et artificielle du carbone," in which he showed that carbon bisulphide is decomposed by a couple formed of gold-leaf wrapped in tin-foil. We repeated this work and when the carbon bisulphide was pure, there was no deposit formed in five years. When, as in Lionnet's experiment, moist carbon bisulphide was used, small, bright particles were observed deposited on the vessel at a low temperature; these bright particles were formed by drops of water which, at first sight, could be taken for small crystals. We then studied what the necessary conditions were in order to precipitate carbon by electrolytic decomposition, and showed that carbon thus prepared is always amorphous.

On February 19, 1880, J. B. Hannay published a preliminary notice bearing the title "On the Artificial Production of the Diamond,"[1] and a little later a paper "On the Artificial Forma-

[1] Proceedings Royal Society, Edinburgh (1880), p. 188.

tion of the Diamond."[1] In this work Hannay undertook the study of carbon separated from the hydrocarbons by the action of the alkali metals. It has been known for a long time that this reaction, at a high temperature, gives a bright carbon, possessing some hardness. Hannay first worked with paraffin oil, and in experiments which were varied somewhat, but obtained no results. He then tried a more complex body, bone-oil, to which he added 10 per cent. of oil of paraffin. The alkali metal chosen by Hannay was lithium.[2] He heated the whole founteen hours in an iron tube, whose ends had been welded and when the tube was not broken, he sometimes found small, black or transparent crystals which possessed the properties of the diamond and burned in oxygen, giving a weight of carbonic acid proportional to the atomic weight of carbon. Hannay, on collecting the gases of combustion, observed that the carbonic acid formed contained 3 per cent. of nitrogen, and he says that since the diamond has only been obtained in the presence of nitrogen compounds and from the fact that the mixed product (1 part only of 14 mm. was transparent) contained nitrogen, he is led to believe that it is by the decomposition of a nitrogenous body and not from a hydrocarbon that the diamond is produced in this reaction.

The work of Hannay is somewhat complicated and contradictory. The manner of separating the diamond from the layer of carbon which covered the iron tube is not very clear. In one experiment he found on the bottom of the tube a smooth coating adhering to the sides. Since he never obtained the result, he sawed off the end of the tube. The mass was black, and on removing it with the chisel, it appeared to be formed of iron and lithium. He pulverized it in the mortar when hard particles were observed which did not resist a blow. On examination it was found to be transparent, and was the diamond. It appears that the mass which was removed by the chisel lost the diamonds which it contained very easily in the mortar. Moreover, at the same time Hannay mentions the presence of silica which should not be found in these experiments. If the substance obtained by Hannay

[1] Proceedings Royal Society, Edinburgh (1880), p. 450.

[2] Hannay does not give the preparation of the lithium which he used in his work. Before the investigations of Guntz, it was impossible to obtain lithium from chemical dealers.

was really diamond, it was formed under pressure as we shall see later, by the solution of carbon in an easily fusible alloy of lithium and iron, and not by the action of the nitrogenous bodies in the bone oil.

At all events I desired to repeat the work of Hannay. I drew out wrought iron which had the following dimensions: Length, 0.60 meter; thickness, 0.014 meter; internal diameter, 0.006 meter. Inside the tube was introduced a mixture of lithium (for which I am indebted to Gunz), bone-oil and oil of paraffin. But when I sealed the tube by welding the iron at a red heat (as Hannay states) I observed that all of the liquid contents of the tube distilled before the tube was entirely closed. Also when the tube was wound with a lead coil, cooled by a current of cold water, the temperature obtained at the end in attempting to seal, would not permit the mixture to remain in the tube.

After many unsuccessful attempts I abandoned the attempt to repeat the experiments. In this direction Marsden has published very interesting experiments in the same line, which we shall review.

In a preliminary notice, on the preparation of adamantine carbon, Marsden[1] remarked that he heated silver or an alloy of silver, or an alloy of silver and platinum in a crucible of sugar carbon to the melting-point of steel. At this high temperature, silver dissolves a small quantity of carbon which, on cooling, separates.

Marsden treated the metal with nitric acid, and, in the residue, collected amorphous carbon, graphite, and small, black or transparent crystals. The quantity thus obtained was much too small to burn in oxygen and weigh the carbonic acid. According to Marsden, the properties of these crystals resemble those of the diamond. At the end of the paper Marsden announced that he was continuing the experiments, but since then he has given nothing further. The work of Marsden is curious, since he correctly observes a large number of different products and crystals which can be formed at the moment of solidification of a mass of silver, which gives up oxygen, alumina, silica, etc. For example, in some work in which he studied the solubility of silica in silver[2]

1 Proceedings of the Royal Society, Edinburgh (1880–1881), p. 22.

2 "On the Crystallization of Silica in Fused Metals," Proceedings of the Royal Society, Edinburgh (1880–1881), p. 57.

he speaks of hexagonal plates of a light yellow color, which were mistook at first for graphite and which were not studied further. These hexagonals were crystalline silicide of carbon, SiC, which is readily formed in silver at a high temperature, and which at present is prepared industrially under the name of *carborundum*.

To return to the work of Marsden, which I have frequently repeated, I believe that it is possible to obtain, in such an operation, black diamond more or less crystalline. This is the case when the crucible, lined with retort carbon, is heated in the wind-furnace. It is known that this substance contains only a little ash; the fire is quickly drawn, and a current of air, due to the strong draft of the chimney, rapidly rushes through the furnace. The crucible is rapidly cooled. The silver contained in the Doulton crucible of graphite is cooled on the outside; a metallic shell of great resistance is formed, while the center of the crucible is still liquid. On passing from the liquid to the solid state, it increases in volume, compressing the small quantity of carbon which remains in solution and which is about to deposit. Under the action of this pressure, black diamonds are formed. Previous to this point all the excess of carbon has been deposited as graphite.

We shall see later that this experiment on the formation of black diamond in silver gives good and constant results, by quickly cooling a small quantity of silver saturated with carbon. By this method we never obtained transparent diamonds. The black residue separated by treating the silver with nitric acid, then with sulphuric acid and finally with hydrofluoric acid, is a mixture of graphite, black diamonds and transparent crystals, which at first sight it is possible to mistake for diamonds. The graphite was brought into a state of graphitic oxide by potassium chlorate and nitric acid, then destroyed; but the transparent crystals disappeared when the residue was fused with potassium bisulphate. On the contrary, the black crystals remained and showed the properties of black diamond. Marsden no doubt obtained the black diamond, but accidentally and without noting the important part played by the pressure.

In conclusion, I repeat that the results of Marsden are very

curious and I have had the occasion to verify some of them in my work. In particular, I have readily obtained the crystals of silica that he has mentioned in the paper quoted.

A. Preliminary Investigations.

Our early work on fluorine and its compounds brought about some experiments on the crystallization of carbon. It is known that fluorine is a great mineral former and that it frequently forms well-crystallized bodies in the reactions in which it enters. We therefore first studied the combinations of fluorine with carbon which have not been known heretofore. We prepared various fluorides of carbon and varied the conditions, hoping that in an inverse reaction we would obtain crystalline carbon.[1]

In all of this work on the decomposition of the fluorides of carbon we never obtained anything but lampblack at dull redness or graphite at a high temperature. We were led to generalize our work and to undertake, as we shall show later, as complete a study as possible on the three varieties of carbon.

In order that this should include the diamond we thought, in the beginning of our work, that a number of preliminary experiments should be systematically undertaken, with the view of producing crystalline carbon. In all problems of research the plan is the same, and work of analysis should precede that of synthesis. In this particular case it appeared important to make as complete a study as possible, not only of the properties of the diamond, but also of the geological conditions under which it has been formed. Hence we will take up the preliminary work at once.

On Some New Properties of the Diamond.—Those who have studied the properties of the diamond have directed their attention particularly to the action which oxygen exerts on this substance at a high temperature. Although the action of oxygen has been known for a long time, there has been no study of the exact temperature of combustion of the diamond. In the determinations of the atomic weight of carbon, Dumas and Stas[2] made their experiments in a porcelain tube heated to redness in a clay furnace. Most chemists since this time, who have burned the

[1] H. Moissan : "Action du fluor sur les différentes variétiés de carbone," *Compt. rend.*, 110, 276 and 951 (1890).

[2] Dumas and Stas : "Recherches sur le véritable poids atomique du carbone," *Ann. chim. phys.*, 3e série, I, 5.

diamond, have used this method of combustion in a porcelain tube in a good combustion furnace such as is used in organic analysis.[1] In the beginning of our work we observed that there is a great difference in the combustion point of different specimens from Brazil or from the Cape.

In order to determine the combustion point, we used the electric pyrometer of Le Chatelier, which was placed in a porcelain tube that was glazed inside and outside. The alloy was placed on a small platinum support which contained the diamond to be burned. This apparatus, closed at each end by glass stoppers, cemented to the porcelain tube, permitted the combustion of the diamond in oxygen to be observed.[2]

Two small drops of baryta water were placed in the apparatus, the one after the oxygen in order to insure its purity, the other after the porcelain tube, to determine when the combustion began. When the temperature was raised the combustion of the diamond, recognized by the action of the carbonic acid on the baryta water, proceeded slowly at first and without apparent production of light, but when the temperature was raised 40° to 50° the combustion was accompanied by light and the diamond was surrounded by a distinct flame.

Another curious fact was observed in these experiments. During the combustion of the diamond there was always observed to appear on its surface small, opaque particles, which indicate the transformation of the transparent into black carbon, while at the same time the combustion continues. The results of our experiments are as follows:

No. 1 Ochre-colored carbon; burned with flame at a temperature of 690°.

No. 2. Very hard, black diamond, having a rough appearance; burned with flame between 710° and 720°.

No. 3. Transparent diamond from Brazil; began to burn without flame at 760° to 770°.

No. 4. Well-crystallized, transparent diamond from Brazil; began to burn without light between 760° and 770°. This diamond,

[1] Friedel: "Combustion du diamant," *Bull. Soc. Chim.*, **41**, 100.

[2] The oxygen was prepared in the laboratory from a mixture of potassium chlorate and manganese dioxide, the latter having been first strongly heated. Before each combustion, this oxygen was tested with potassium pyrogallate. It should not contain more than 3 per cent. of other gases.

which weighed about 1 carat, was previously heated in a carbon lining at the temperature of an oxyhydrogen blowpipe, and was covered with a thin, black layer which was not affected by aqua regia. This superficial layer disappeared a little before the combustion of the diamond.

No. 5. Cut diamond from the Cape; began to burn without light at 780° to 790°.

No. 6. Bort from Brazil; began to burn without light at 790° and burned with flame at 840°.

No. 7. Bort from the Cape; burned without light at 790° and with flame at 840°, like the preceding sample.

No. 8. A piece of bort which was so hard that it was impossible to cut, and scratched the steel wheel without being cut by diamond dust, began to burn only at 800° and with flame at 875°.

We then studied the action of various gases on the diamond. These experiments were made with gases prepared with the greatest of care and especially free from oxygen. The diamond on which the experiment was made was placed in a small, platinum boat in a platinum tube. Cut and transparent diamonds were used to better observe the least chemical action. Heated in hydrogen to 1,200°, the Cape diamonds did not change in weight. Moren has shown that diamond is not altered in hydrogen at a white heat.[1]

When the slightly yellow, cut stones were used, very frequently a slight change of tint was observed; they became light and took on a paler yellow color. But sometimes also they lost their brilliancy and became milky. Diamond heated to redness in a current of fluorine did not change in weight, while graphite was attacked at dull redness and lampblack at the ordinary temperature.[2]

Dry chlorine did not act on the diamond between 1100° and 1300°; it was without action on the cut Cape diamond, which neither changed in weight or color. The same is true of hydrofluoric acid gas under the same conditions.

Sulphur vapor only attacks the diamond with difficulty. It must be heated to 1000° (determined by the electric pyrometer) for

[1] Moren: *Compt. rend.*, **70**, 990.

[2] Henri Moissan: "Action du fluor sur les différentes variétés de carbone," *Compt. rend.*, **110**, 276.

reaction to take place. With the black diamond, carbon bisulphide is formed at 900°.

Sodium vapor is without action on diamond at 600°. Iron, in the liquid state, energetically unites with the diamond and gives a fusion which, on cooling, deposits graphite. Melted platinum also combines with diamond at a high temperature. Bisulphate of potassium and the alkaline sulphates do not attack the diamond when fused with it. This is true of calcium sulphate, which is not reduced at 1000°. The action of oxidizing bodies has already been carefully studied. It is sufficient to recall the separation of the different varieties of carbon as shown by Berthelot, by means of potassium chlorate and nitric acid. In a valuable paper Ditte[1] has shown that at 260° anhydrous iodic acid attacks all the varieties of carbon except the diamond. Fused potassium chlorate, as well as nitrate, are without action on the diamond, while black diamond, as Damour has shown, is attacked under these conditions.

A curious reaction is shown by the alkaline carbonates. When diamond is introduced into fused sodium or potassium carbonate having a temperature of 1000° to 1200°, it rapidly disappears, forming carbon monoxide. This reaction induced us to investigate whether the diamond did not contain a small quantity of hydrogen, in which case it would come off in gaseous form and could be readily recognized.

The experiment was conducted as follows: A platinum boat, containing the perfectly dry alkaline carbonate and the diamond, was placed in a porcelain tube, glazed inside and outside and which was exhausted after having previously been filled with carbon dioxide. The tube was heated to 1100° to 1200° and the gases evolved were collected for analysis.

A potash solution removed the carbon dioxide. The carbon monoxide was absorbed by a solution of cuprous chloride; the small residual gas, after adding oxygen, did not change in volume under the action of the spark. From this experiment it can be concluded that the diamond worked with, contained neither hydrogen nor gaseous hydrocarbons. We believe, however, that this

[1] A. Ditte: "Recherches sur l'acide iodhydrique et ses principau composes metalliques," Thèse de la Faculté des Sciences de Paris, 1870.

work is worth repeating with a larger quantity of diamond and particularly with the variety of diamond which fluoresces so beautifully in a blue light. These fluorescent diamonds probably contain a trace of hydrocarbons.

We conclude from this preliminary work that the temperature of combustion of diamond varies with different specimens, it being between 760° and 875°. In general, the harder the diamond, the higher is its temperature of combustion. This variation of the combustion point establishes the existence of many varieties of diamond-forming carbon. The diamond at 1200° resists the action of chlorine, hydrofluoric acid, and of various salts; on the contrary, it is readily attacked at this temperature by the alkaline carbonates, and this decomposition shows that the specimens examined contained neither hydrogen nor hydrocarbons.

Analysis of the Ash of the Diamond.—In our first work we deemed it necessary to determine the material which formed the ash of the diamond. Dumas has remarked that it is well to know the traces of impurities contained in the crystals in order to know from what surroundings the carbon can have crystallized.

Since the quantity of ash is very small in the very clear crystals, I directed my attention to bort which is much less valuable and which contains more of the impurities than do the colorless stones. The method of analysis varied with the substances contained. Micro-chemical reactions were of the greatest value in some tests. We also used spectroscopic analysis, but the presence of iron, which in the spectroscope gives a large number of lines, complicates this method. This method served to establish the existence of traces of elements that could not be detected by micro-chemical means.

Iron was detected by potassium sulphocyanide. Either a sulphuric or hydrochloric acid solution of the ash was used or an acid solution after fusing the ash with a little pure sodium carbonate.

Silica was detected by means of a salt of phosphorus bead. A trace can be recognized as insoluble silica in the bead. This is the most delicate reaction that we found for this substance.

Titanium was detected by means of the reaction of Léwy, by the action of titanic acid on a solution of morphine in sulphuric acid.[1]

[1] Léwy: "Contribution a l'Étude du titane," Thèse de la Faculté de Paris, 1891, and *Compt. rend.*, Nov. 29, Dec. 13, 1886.

The ash can be either directly treated or it may first be fused with bisulphate. Calcium was recognized with the microscope by means of calcium oxalate crystals. Magnesium was likewise recognized under the microscope, by the formation of magnesium ammonium phosphate. All the pieces of diamonds before being burned in oxygen, were treated with hydrofluoric acid, then with boiling aqua regia, finally washed with water, and dried in an air-bath. The weight of the ash is not given when under one-half a milligram.

No. 1.—Bort from the Cape; greasy appearance, violet color, indistinct crystals. Sp. gr. =3.49, W = 0.387, ash, 0.0005 equivalent to 0.13 per cent. of the bort. The ash was white, with yellow particles; it was very light and preserved the general form of the crystals, with a general appearance of opened leaves.

Iron.—Considerable, recognized directly and readily by solution of the ash in hydrochloric acid.

Silica.—Very good reaction in the bead.

Calcium.—Traces as calcium oxalate confirmed by the spectroscope.

Magnesium.—Distinct but weak reaction as magnesium ammonium phosphate.

No. 2.—Two pieces of bort from the Cape; greasy appearance, pointed crystals, iron-gray color. Sp. gr. = 3.49, W = 0.146. Very little ash, less than one-half a milligram by weight, yellow colored and preserving the original form of the crystal. Rich in iron. Good silica reaction in the bead. No titanium. Traces of calcium and magnesium.

No. 3.—Bort from the Cape; iron-gray appearance. Sp. gr. = 3.48, W = 0.093. Very little grayish white ash. Iron, characteristic reaction; silica, good reaction.

No. 4.—Bort from the Cape; cubic form, curved faces. Sp. gr. = 3.48, W = 0.100. Good reactions for iron and titanium.

No. 5.—Bort from the Cape (Kimberly); bright, greasy appearance. W = 0.212. White ash, slightly yellowish on the edges. Iron, distinct; no titanium.

No. 6.—Bort from the Cape (Jaegersfontein); reddish color, greasy appearance. W = 0.272. Considerable yellow ash. Silica; much iron; titanium distinct.

No. 7.—Black diamond from Brazil; very hard, and having the appearance of anthracite. Sp. gr. = 3.50, W = 0.0397. The weight of the ash was less than one-half of a milligram, but was comparatively greater than that from No. 3. The ash was of a brick-red color, very hard and had a granular appearance.

Iron.—Clear reaction, formed the greater part of the ash, recognized by ferrocyanide and by the borax bead.

Calcium.—Very small quantity, detected by the spectroscope.

Magnesium.—Doubtful.

Titanium.—None.

No. 8.—Black diamond from Brazil; black color, distorted appearance, showing alternate black and white striations under the microscope. W = 0.354. It gave, on combustion, an ash of 0.017 or 4.8 per cent.

It was possible to make a quantitative analysis of the ash; the results are as follows:

	Per cent. of the ash.	Per cent. of the diamond.
Ferric oxide	53.3	2.2
Silica	33.1	1.4
Lime	13.2	0.6
Magnesia	traces	traces

No. 9.—Bort from Brazil; red fragments. Crystalline surface containing transparent veins of yellow color. Sp. gr. = 3.49, W = 0.130. Less than one-half a milligram of ash, appearing as yellow and white leaves. This ash was more difficultly attacked than that of the black diamond and had to be fused with potassium carbonate.

Iron.—Clear reaction with sulphocyanide and ferrocyanide.

Silica.—Rich in the bead reaction.

Magnesium.—Doubtful.

Calcium.—Very little.

Titanium.—None.

No. 10.—Bort from Brazil; green, transparent fragments, highly refracting, presenting some good crystalline faces. Sp. gr. = 3.47, W = 0.093. The ash was small and had a slight yellow color. Only the perfectly crystalline diamonds gave small quantities of ash.

Iron.—None.

Silica.—Good reaction in the bead.

No. 11.—Cut diamonds from the Cape; slightly yellowish, very clear and fluorescent. Sp. gr. = 3.51, W = 0.126. The ash was barely visible; iron could be recognized.

All the specimens of bort or diamond from the Cape that we examined contained iron. This metal furnishes the major portion of the ash. We found it in the ash of the black diamond and the ordinary diamond of Brazil, except in one green-colored variety of bort where it was entirely absent. In all of the specimens, we found silica and in most, calcium. Daubrée observed the presence of this alkaline earth in certain irons, as that of the Ovifack.

Investigation of the Blue Ground of the Cape.—The diamonds of the Cape of Good Hope are found in the large mines in a serpentine breccia which contains more than eighty minerals and carries only 100 milligrams to 500 milligrams of crystalline carbon to the cubic meter. At first this blue ground was searched only for diamonds of some size and which could be picked out by hand. When the method of treatment was changed and machinery replaced the work of man, it was possible to separate, by means of a fine sieve, much smaller diamonds; but, at present, the presence of microscopic diamonds in the serpentine rocks is ignored. These latter, of little importance from a commercial standpoint, are particularly interesting in the subject of the artificial preparation of this variety of carbon. I am obliged for this work to the kindness of de Monmort, who at the last Paris Exposition procured for me the material necessary for this work. The samples were from the Old de Beers Mine.

In order to isolate the microscopic diamonds which occur in this serpentine it was necessary to decompose all the other minerals which accompany this precious stone.

Two kilograms of the blue ground were divided into portions of 250 grams and treated with an excess of boiling sulphuric acid for twelve hours. On cooling, it was washed with water, and treated with aqua regia. Another washing removed a large quantity of soluble portion; the residue was placed in a platinum capsule and treated with an excess of boiling hydrofluoric acid. The residue which remained was 100 grams; the larger unattacked portions and the larger rubies were removed with pincers. It was

next treated with boiling sulphuric acid, washed with water, then treated with hydrofluoric acid, and this double treatment repeated twelve or fourteen times, in order to remove principally the crystalline alumina which is difficult to eliminate. There remained only 0.094 gram of material and this residue was treated fifteen times with a mixture of potassium chlorate and nitric acid to destroy the graphite. The final residue after washing with hydrofluoric acid, then with boiling sulphuric acid, was fractionated from the point of density of the material which it contained, with bromoform having a density of 2.9 and methylene iodide of 3.4.

The microscopic examination of the residue was followed throughout the whole preparation. Before the treatment with potassium chlorate we were able to recognize the presence of graphite in bright, hexagonal crystals or plates sometimes appearing in small cups. We also found large pieces of some thickness showing triangular impressions. This graphite with potassium chlorate gave a green-colored, graphitic oxide which changed to yellow and which was destroyed by sulphuric acid in order to avoid its transformation into pyrographitic oxide on burning. The graphite of iron, as has been shown by Berthelot, also gives a green-colored, graphitic oxide. We were able to isolate a graphite which sulphuric acid at 200° swelled.[1]

On examining the residue having a greater density than 3.4, which remained at the bottom of the methylene iodide, after these treatments, it was observed under the microscope that it consisted of a number of substances:

1. An amber-yellow substance in irregular masses.
2. Black diamond.
3. Microscopic diamonds.
4. Small, transparent crystals which did not burn in oxygen, appeared as elongated prisms, which did not fluoresce in violet light and which were acted on by polarized light.

These fragments of a yellow substance which resisted such energetic treatment were somewhat transparent, some possessing the rectangular depressions in which crystals may have been included. Heated to 1000°, this material left a gray residue, slightly magnetic and containing a large quantity of iron. We found

[1] We have previously shown in our work on graphite how it is possible to prepare this variety.

the same substance in the cavities of large, natural diamonds and in some of the fusions in which the artificial diamond was prepared.

The fragments of black diamond which we found with the microscope in the blue ground of the Cape were round, rarely scarred; some showed right angles; others had curved angles and resembled octahedrons (Fig. 19, A); some possessed a bright,

Fig. 19. Microscopic diamonds from the Cape magnified 100 diameters.

oily appearance. Black, irregular and pointed fragments were also found. Their density varied between 3 and 3.5; they scratched the ruby and burned in oxygen at 1000°.

The transparent diamonds varied greatly in size; some were scarcely visible under the microscope with 500 diameters. These were rounded and were more numerous (Fig. 19, B). Some had a well-crystallized appearance (Fig. 20, B), and others appeared as transparent drops (Fig. 20, A and C), possessing striations

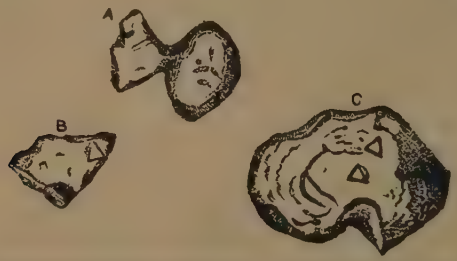

Fig. 20. Transparent microscopic diamonds from the Cape, magnified 100 diameters.

and triangular impressions; they burned in oxygen, giving carbon dioxide and readily scratched the ruby. Along with these diamonds were found, in small numbers, fragments of bort and smoky diamonds. Some of the transparent crystals, which appeared as elongated prisms, contained silica; this could be destroyed, as well as the amber-yellow substance of which we have

previously spoken, by two fusions with potassium bisulphate, then by treatment with hydrofluoric acid and finally with sulphuric acid.

In our study on the blue ground of the Cape, we discovered the existence of numerous microscopic diamonds, bort, black diamond in many forms and varying density, and graphite. The quantity of the graphite contained in the blue ground is certainly greater than the quantity of diamond which it is possible to find, and the crystals of graphite are separated from one another.

In conclusion I would say that the discovery of black diamonds in the blue ground belongs to Couttolenc,[1] who has shown its presence in the Old de Beer's mine. Although my analytical work was ready for two years, I had not published anything on the subject, hence, the priority belongs to Couttolenc.

If this worker has not known of the existence of the microscopic diamonds, it appears, in his treatment of the blue ground, that he made a fusion with caustic soda, which always contains more or less carbonate; I have shown that the diamond is easily destroyed by fusion with the alkaline carbonates.

Investigation of the Diamondiferous Sand of Brazil.—Thanks to Professor Lacrois of the "Museum d'Histoire naturelle," we were able to study the diamondiferous sand of Brazil which contains microscopic diamonds. 4.5 kilos were sifted and gave 1350 grams of a powder formed almost entirely of silica. The treatment was long, and it was only after a dozen treatments, using alternately hydrofluoric acid and boiling sulphuric acids, that a residue of 2 grams was obtained.

The substance was fused with potassium acid fluoride, after which it was treated with potassium bisulphate. The residue contained jagged particles made up of small transparent grains, some spangles of native gold and platinum, and small, bright black crystals, having the appearance of graphite. Some of the latter were separated and converted into graphitic oxide, which, on burning, gave pyrographitic oxide. After recognizing the graphite, the entire residue was treated with methylene iodide. The portion heavier than the methylene iodide was separated and again

[1] "Examen de la terre diamantifère de la mine d'Old de Beers, by Couttolenc" (Société d'Histoire naturelle d'Antun, 5e Bulletin, 127, December, 1892).

treated with potassium acid fluoride, then with bisulphate. One treatment with aqua regia was made to remove the precious metals. We were thus able to separate the black particles and the transparent particles which had no action on polarized light, but completely burned in oxygen, giving a white precipitate in baryta water. The residue also contained bright grains which were affected by polarized light; they had an elongated form, corroded surface, would not burn and could be dissolved only by successive treatments.

The sand of Brazil contains the black diamond with a roughened surface (Fig. 21, B), the transparent diamonds (A and B)

Fig. 21. Microscopic diamonds from Brazil, magnified 100 diameters.

of irregular form, and graphite, as we have shown above. Therefore, there is found in nature, either at the Cape or in Brazil, black or transparent, microscopic diamonds and, in both cases, these particles of carbon having a high density, are accompanied by graphite.

Investigation of the Meteorite of Canon Diablo.—Since the presentation of a paper on the meteorite of Arizona to the Académie des Sciences, by Mallard,[1] we have been able to procure specimens of the meteorite and study the carbon which it contains. We have not published the results and we call attention to the interesting communication of Friedel[2] on this subject. This investigation has shown the existence of black diamond in the meteorite of Canon Diablo. Among the different samples which were analyzed, there was a striking one, weighing but 4.216 grams,

[1] Mallard: "Sur le fer natif de Canon Diablo," *Compt. rend.*, **114**, 812, April 4, 1892.

[2] Friedel: "Sur l'existence du diamant dans le fer météorique de Canon Diablo," *Compt. rend.*, **115**, 1037, December 12, 1892.

which showed a very hard portion on which the diamond steel was without action. On closely examining this specimen, it was seen that the fragment that scratched the steel was surrounded by a black border which was formed of carbon and carbide of iron (Fig. 22).

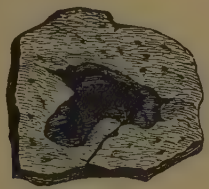

Fig. 22. Meteorite from Canon Diablo, magnified 3 diameters.

This specimen was treated with boiling hydrochloric acid until the iron was removed; a mixture was obtained which contained:

1. A very light carbon in form of an impalpable powder which required twelve hours to sink in water and which perhaps arose from the decomposition of the carbide of iron.

2. A carbon in very thin ribbons, chestnut-colored under the microscope, appearing jagged, and which seemed to have been strongly compressed.

3. A dense carbon which appeared principally as rounded fragments, mixed with small particles of phosphide of iron and nickel, having a golden reflection.[1] This mixture was alternately treated with boiling sulphuric acid and hydrofluoric acid; its density was then so high that part sank in methylene iodide. This last residue was treated eight times with potassium chlorate and nitric acid. The dark-colored fragments slowly disappeared, and at the same time a small quantity of iron passed into solution. Finally, there remained only two yellowish fragments, entirely identical, having a clear and greasy appearance, not possessing triangular impressions, and wrinkled and distorted on the surface; they resembled the distorted crystals of bort.[2] These two fragments sank in methylene iodide, easily scratched the ruby and burned in oxygen, leaving an ash which preserved the form of the

[1] This phosphide of iron and nickel, according to Friedel, possesses all the characteristics of schreibersite.

[2] The lapidaries apply the name of bort to transparent diamonds which show an indistinct crystallization and no cleavage and which are not cut by diamond dust on the steel wheel.

fragment. This ash had a yellow color and it was possible to detect the presence of iron in it.

The larger diamond (Fig. 23) measured 0.7 mm. by 0.3 mm.; it had a yellow color, a rough surface and permitted light to pass through it.

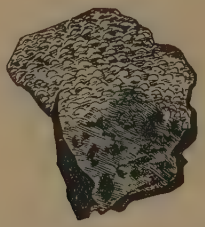

Fig. 23. Transparent diamond from Canon Diablo.

In the other specimen we found, beside the dense carbon mentioned, a mixture of the phosphide and the sulphides of iron and nickel, appearing as a dendritic, crystalline substance, which had a gray color, duller than platinum, and which did not dissolve on treatment with hydrofluoric acid and aqua regia. We also found some fragments of black diamond having roughened or bright surfaces, a density of about 3 and which burned in oxygen at 1000°. These black diamonds should not be confounded with some black particles of magnetic oxide of iron which do not burn in oxygen and are not attacked by sulphuric acid,[1] as is the case with the oxide Fe_3O_4 when it is formed at a high temperature. It is curious to notice what little homogeneity this Canon Diablo meteorite possesses. We took, for example, two samples of the same specimen 1 cm. apart; on analysis, they gave the following results:

	No. 1.	No. 2.
Iron	91.12	95.06
Nickel	3.07	5.07
Silica	0.050	....
Insoluble	1.47	0.06
Magnesia	traces	....
Calcium	none	....
Phosphorus	0.20	....
Sulphur	none	....

[1] In order to effect the solution of the small particles of the stable magnetic oxide, it was necessary to make two successive fusions, of fifteen minutes each, with sodium bisulphate.

The two samples contained carbon in varying quantities, but no sulphur.

Another meteorite of the same kind which contained no trace of carbon showed, in specimens taken several centimeters apart, the following composition:

	No. 1.	No. 2.
Iron	91.09	92.08
Nickel	1.08	7.05
Silica	0.05	....
Insoluble	none	....
Magnesia	none	....
Calcium	none	....
Phosphorus	not determined	....
Sulphur	0.45	....

A third sample of 20.200 grams gave three particles of black diamond, but no transparent diamond. The piece of the meteorite of Canon Diablo which I studied contained the transparent diamond, the black diamond and a brown carbon of less density. Also in certain samples I was able to recognize the presence of graphite in the form of small masses having a greasy appearance. This graphite was transformed into graphitic oxide which could be recognized with the microscope and which burned on raising the temperature. The transparent diamond, therefore, can be found in other planets than the earth if the iron of Canon Diablo is a meteorite; in this specimen it is found in the midst of the metallic mass.

Iron from Novy-Urej, Krasnoslobodsk Government of Penza, Russia (fell August 23, 1886).—Small specimen, dark in color, under the microscope showed some bronze-colored points; it weighed 0.410 gram. This meteorite is carbonaceous but not holosidereal. It is known that this is the first meteorite in which Jerofeïeff and Latchinoff discovered the existence of the black diamond. The treatment with dilute hydrochloric acid was somewhat slow, and subsequently it was found, on examining the residue under the microscope, that the meteorite is rich in silicious matter. On the first treatment with boiling sulphuric acid the material was disintegrated, and on fusing with potassium acid fluoride all of the silicious matter disappeared. With the microscope, small masses of a dark color could be seen.

After the treatment with potassium chlorate and nitric acid we did not find, either under the microscope or by burning, a trace of graphitic oxide. It must not be forgotten, however, that the sample that we studied weighed less than half a gram.

After treating again with potassium acid fluoride, then with boiling sulphuric acid, we found under the microscope a dark-colored residue having the appearance of black diamond and being agglomerated into small, granular masses. All of these black grains burned in oxygen at 1000° and a small, transparent grain, which had resisted all of these treatments, was found intact after the combustion. These small particles of black diamond sank in methylene iodide. These experiments confirm those of Jerofeïeff and Latchinoff. The iron of Novy-Urej contains the black diamond.

TECHNIQUE OF THE INVESTIGATIONS.

In undertaking the separation of a mixture of the different varieties of carbon with all of the bodies that inorganic chemistry can furnish, the solution of the question, at first sight, appears almost impossible. It is, however, easy to separate a fraction of a milligram of diamond from a kilo of other substances. We have given such an example in the study of the blue ground of the Cape.

Diamond and graphite are sufficiently refractory to the most of reagents so that repeated treatment with concentrated hydrofluoric acid, then with boiling sulphuric acid, is powerful enough to remove the most of the mineral substances. All of the silicates readily disappear. Fused or crystalline alumina and crystallized aluminum fluoride are attacked, disintegrated and dissolved. When such a compound as titanic acid is present it is well to treat with nitric acid, then with ammonia. The solid residue is always washed by decantation. When substances other than the diamond have been destroyed, or where they exist only in traces, the graphite is transformed into graphitic oxide and by this method of separation, which we owe to Berthelot, the diamond remains as the last residue.

Berthelot mixes the different kinds of carbon with potassium chlorate and nitric acid into a thick paste and maintains the whole at 60° for five or six hours. This treatment, repeated six or

eight times, brings about the complete transformation of the graphite into graphitic oxide. This was then burned by heating to dull redness. The pyrographitic acid thus obtained was destroyed by treatment with nitric acid and potassium chlorate.

As our intention in this work was not to study and compare the different graphitic oxides, we modified the analytical method of Berthelot in the following manner: All of the amorphous carbon was destroyed at the beginning by means of nitric acid or aqua regia; it was then washed with water (always by decantation), dried and the mixture, without being pulverized, was introduced into a small glass flask by means of a badger hair-brush.

If there was only a small quantity of graphite, about 2 grams potassium chlorate were added. The whole was mixed in the flask and 8 or 10 cc. of concentrated nitric acid were added. The flask was allowed to remain on a water-bath at a temperature of 60° to 80° for a day. It was then washed with boiling water, dried in an oven and the same proportions of chlorate and acid were again added to the flasks. The second treatment took place over night at a temperature of 60°. This treatment was continued until all of the graphite was converted into graphitic acid.

By carefully destroying all of the amorphous carbon before the oxidation, we never had an explosion. By using a large excess of nitric acid, we had the advantage, when there was only a little graphite, of dissolving it or suspending it in gelatinous form in the liquid. The graphite in that case was removed by decantation. If, on the contrary, the quantity of graphite was large, it could be transformed into graphitic oxide, when it was destroyed either by burning or by prolonged treatment with boiling sulphuric acid. The rapidity of oxidation of any graphite varies with the concentration of the nitric acid. In our first work we used the ordinary concentrated nitric acid and repeated the treatment many times. Later, we used concentrated nitric acid obtained by the decomposition of dried potassium nitrate with a large excess of sulphuric acid and which was exactly a monohydrate. Under these conditions, as we showed in our study of graphite, the operation was much more rapid. In the more lengthy operations we avoided as much as possible changing the vessel. When the graphite was detroyed in the small flask of which we have spoken,

in order to obtain the traces of diamond which it contained, it was completely filled with water, the mouth closed with the thumb and inverted into a dish containing water. By virtue of its density, the heavy powder rapidly collected on the bottom of the capsule.

To examine this powder a narrow tube was used in form of a pipette; the upper end was closed with the finger and the point was placed near the particles on the bottom of the dish. On raising the finger the atmospheric pressure projected the powder in the tube with the liquid and it could be subsequently deposited on a glass slide for examination under the microscope. According to the manner in which it sinks in the liquid its high or low density is known. After the microscopic examination, the glass slide and the cover glass were washed into a dish with a jet of distilled water. This microscopic examination shows that in spite of all the precautions these residues always contain small fragments of glass from the vessels or the liquids. When the laboratory contains a lamp for glass-blowing, powdered glass always remains in the atmosphere and can be found on the bottom of glassware or dishes.

Small grains of silica, having a bright fracture or rounded surface, were also found in this residue; to avoid this, care should be taken to crystallize in closed vessels the potassium chlorate used in the destruction of the graphite. For the same reason the vessels containing the acids ought not to be shaken, nor the liquid at the bottom of them used.

This constant presence of glass and silica in the residue necessitated a final treatment with boiling hydrofluoric acid. To this end, the slight residue which remained in the dish was washed with a jet of water into a platinum capsule. The excess of the liquid was decanted and 50 per cent. hydrofluoric acid was poured on the wet particles. This acid was prepared pure in the laboratory by heating potassium acid fluoride in a platinum retort. The acid liquid was kept just a little below its boiling-point for two or three hours. It was then allowed to cool, and washed with water by decantation. Sometimes the residue increased and under the microscope there could be seen regularly formed crystals of fluorides insoluble in excess of acid. It was necessary to treat

with boiling sulphuric acid for several hours to destroy those compounds. After cooling, the acid was diluted with water and another treatment made with hydrofluoric acid. After washing with water the volume of the residue was considerably diminished. In these treatments, care was taken not to allow the slight residue to become completely dry, that is, not until the end of the operation, when it was dried on a platinum dish in the air-bath. The residue was then treated with methylene iodide having a density of 3.4, in which the diamond readily sank.

It is necessary to leave these particles in contact for several hours with methylene iodide, shaking occasionally, the operation being performed in a small test-tube closed with a cork. We also made use of bromoform, having a density of 2.9, to separate the different varieties of carbon. When the fragments of carbon and diamond have been treated with chlorate frequently, they are not wet by water and other liquids. As soon as the surface of the powder is perfectly clean, they swim on the water by capillarity and frequently are thrown, only with difficulty, to the bottom of the glass which is filled with the liquid. It is well to spray the surface of the liquid with absolute alcohol. We frequently lost small diamonds by this phenomenon of capillarity.

B. Solubility of Carbon in Some Simple Bodies at the Ordinary Pressure.

In a preceding chapter we have shown that if carbon was prepared at low temperatures, that is to say, from + 20° to + 200°, it was always amorphous. As a result of this work, we endeavored to separate carbon from a solvent by simple change of temperature. The best solvent for carbon is fused iron, and it was with it that our first experiments were made. Beside this element, a number of other metals possess the same property. Few examples were known and the work had been done between too limited temperatures. The use of the electric furnace has enabled us to extend the observations. Finally, we varied the nature of the solvent, hoping to obtain some differences in the property of carbon thus prepared.

Silver.— Our first experiments with silver were made at 1000°. Pure silver, fused in a cover of sugar carbon, does not perceptibly dissolve carbon. The fusion, treated with nitric acid,

left a slight residue which was carefully studied under the microscope. When a Doulton crucible is used or when the crucible of gas carbon contained silicates, we frequently found the crystal piles of silica, described by Marsden, and of which we have spoken at the beginning of this work. When the carbon crucible was treated with chlorine, or if the silver was fused under a layer of sodium chloride, on examining with the microscope there were found bright crystals, heavy refracting, insoluble in nitric acid and in water, and which could remain many hours in dilute ammonia without perceptibly dissolving. In polarized light they appeared isometric. They were small crystals of silver chloride which in turn were soluble in ammonia, and were immediately decomposed by boiling sulphuric acid.

If silver is heated in the presence of sugar carbon, at the temperature of the forge, it dissolves a small quantity of carbon, and after treating with nitric acid, the residue when examined with the microscope shows amorphous carbon and graphite. If the crucible or the brasque lining contains silica, there are obtained small, yellow or transparent crystals, somewhat strong, of carbon silicide. This substance scratches the ruby, resists all the acids, including hydrofluoric, and has been sometimes taken for the diamond; its appearance, its action on polarized light, the incomplete combustion in oxygen at 700° and its being attacked by alkalies easily serves for its detection. In order to obtain a higher temperature we invented our first electric furnace of quicklime, which from other standpoints has rendered so much service.[1] By means of this apparatus we have been able to heat a metal to 3500°. We have noted that at the boiling temperature silver dissolved a small quantity of carbon and that on cooling, it separated under the form of graphite.[2] After dissolving the metal in nitric acid, then treating the residue as we have already indicated, we never obtained a residue visible with the microscope; all of the graphite, after transformation into graphitic oxide, was destroyed, and no powder remained which would sink in methylene iodide. This experiment was repeated, but the result was always the same.

[1] "Description d'un nouveau four électrique," *Compt. rend.*, **115**, 1031, Dec., 1892, and *Ann. chim. phys.*, 7e série, IV, 365.

[2] At high temperatures, silicide of carbon readily forms in this metal. H. Moissan: "Sur la préparation du siliciure de carbone cristallise," *Compt. rend.*, **117**, 425.

Iron.—When iron is saturated with carbon between 1100° and 3500° there is obtained, on cooling, different results, depending on the temperature to which the mass has been heated and according to the rapidity of cooling. If it has not been heated to more than 1100° or 1200°, there remains, after the first treatment with the acids, a mixture of amorphous carbon and small crystals of graphite. At 3500°, the main product is beautifully crystallized graphite. When the graphite is prepared at a high temperature, it reflects light as strongly as the mirror of the microscope, and at first sight, appears transparent.

Between 1100° and 3500°, liquid iron acts as a solution which dissolves more and more carbon in proportion to the increase of temperature. This explains the formation of graphite in the strongly heated cast iron of the blast-furnace which, on passing from 1700° to 1100°, at which point it solidifies, gives an abundant crystallization of graphite.

In many experiments on fused cast iron, either at the temperature of the forge or at the temperature of the oxyhydrogen blowpipe, or in the electric furnace, I always obtained graphite, the properties of which have already been given.

Aluminum.—The solubility of carbon in aluminum can be readily demonstrated at the temperature of the electric furnace; it commences at the temperature of the forge. It is also possible to prepare a transparent aluminum carbide in yellow crystals leaving the formula Al_4C_3, which is slowly decomposed by water, giving pure methane gas. At the same time that this carbide is formed, the excess of aluminum, or the fused carbide, deposits beautiful crystals of graphite, but nothing else.

Glucinum.—Glucinum carbide prepared by Lebeau, in the electric furnace, readily dissolves carbon at a high temperature. After treatment with dilute hydrochloric acid it gives graphite.

Chromium.—We have had occasion to prepare in the electric furnace 20 kilos of this metal under various conditions. Fused chromium readily combines with carbon at a high temperature and gives two carbides, Cr_4C and Cr_3C_2. By further elevation of the temperature these compounds dissolve large amounts of carbon, which subsequently deposits as graphite which crystallizes in small mirror-like leaves.

Manganese.—Manganese rapidly dissolves carbon at the temperature of the electric furnace. As this metal is very volatile, it is possible to remove the excess of manganese as vapor and collect the crystallized graphite. After treatment with acids, then with the oxidizing mixture, this graphite leaves no residue.

Nickel.—This metal in the electric furnace behaves like iron in the presence of carbon. It appears to dissolve a somewhat less quantity.

Cobalt.—Cobalt also dissolves carbon which it deposits as graphite.

Tungsten.—Tungsten, prepared in the electric furnace, by acting on a mixture of the oxide and carbon, in which the latter is not in excess, does not take up carbon and can be readily polished.

In the first experiment a metal was obtained free from carbon. This experiment was made in a carbon crucible as tungsten is difficultly fusible and in order that the metallic mass, which weighed about a kilo, would remain in the form of a sponge, touching the crucible only at points. This tungsten was very pure as shown by the spectroscope.

If this metallic sponge is further heated by a powerful current, it fuses, then combines with the carbon of the crucible and forms a carbide, W_2C, which dissolves so much carbon that it deposits it as graphite on cooling.

Molybdenum.—In the electric furnace molybdenum dissolves more carbon than does tungsten. It is, moreover, a little more fusible and gives a carbide having the formula Mo_2C. When the temperature falls, the carbon, which is in solution, separates as graphite.

Uranium.—Uranium, which is more fusible than the two preceding metals, approaches iron in the point of solubility of carbon. On cooling, it produces considerable graphite. It should not be forgotten that uranium is somewhat volatile, and if heated long, a large quantity of the metal is lost. Uranium gives a definite and crystalline carbide, having the formula Ur_2C_3.

Zirconium.—Zirconium also dissolves carbon which it deposits as graphite which remains enclosed in the metal. This is due to its high melting-point. As soon as the arc is broken, the outside of the metal solidifies and the graphite cannot rise to the surface.

On treating zirconium carbide, ZrC, with acids it is found that the excess of carbon contained is only as graphite.

Vanadium.—Vanadium deports itself like zirconium. It is difficultly fusible, and the carbon which was dissolved, crystallized as graphitoidal leaves in the midst of the carbide, VC.

Thorium.—The golden yellow, crystalline thorium carbide, ThC_2, can dissolve enough graphite so that, on solidifying, crystals of graphite separate out. It gives no other variety of carbon.

Alkaline Earth Metals.—The carbides of the alkaline earths, CaC_2, BaC_2, SrC_2, when kept in liquid condition in the electric furnace, dissolve carbon which separates as graphite. This is likewise true of the carbides of cerium, CeC_2, lanthanum, LaC_2, and yttrium, YtC_2.

Titanium.—Liquid titanium carbide in the electric furnace is a pasty body which readily climbs up the sides of the crucible. It does not show the great liquidity on fusion, that molybdenum, tungsten, or iron do. This element gives a definite carbide, TiC. By elevating the temperature sufficiently high, this substance can dissolve carbon, which subsequently separates as graphite, either on the surface, or in the interior of the titanium.

Platinum.—At the moment when platinum commences to boil in the electric furnace, it dissolves carbon, which it throws out again below its point of solidification, as graphite. It is possible to thus obtain clearly defined and well-formed crystals. This graphite swells as we have shown before. Iridium, palladium, and rhodium, give the same results.

Silicon.—We prepared crystalline silicon as pure as possible by the method of Deville and fused it into globules the size of a hazel-nut at the temperature of the forge. In order that this experiment should succeed, it is necessary to avoid the action of nitrogen and enclose the crucible in a layer of titanic acid and carbon. A small fragment of sodium can also be added to the silicon, which lowers the melting-point of the element and more easily forms large globules. Fused crystals of silicon were placed on the bottom of a small crucible of retort carbon and covered with powdered sugar carbon. After the first fusion, the globule was

heated again inside a covering of sugar carbon either in the wind-furnace or in the forge.

After cooling, the globules were broken, and in their interior, graphite was found and small geodes coated with bright crystals. These crystals could be separated by dissolving the fusion of silicon in a mixture of nitric and hydrofluoric acids. They frequently were several millimeters long, readily scratched the ruby, and had a density of 3.12. There is thus obtained carbon silicide which was first prepared in the amorphous state by Schützenberger. On repeating this experiment in the electric furnace, the yield of carbon silicide was much greater and it was mixed with no other variety of carbon.

In all of the previous work, the fused elements which dissolved carbon were treated by an acid or an appropriate mixture of acids and the residue treated by the method described in the chapter, "Technique of the Investigations."

The graphite was converted into graphitic oxide, then destroyed, and this treatment was pushed far enough so that all of the corundum, which was frequently found in these fusions, should entirely dissolve.

After the complete series of operations there remained absolutely nothing in the field of the microscope. We never obtained black or transparent fragments which were not attacked, and which sank in methylene iodide, that might be taken for the diamond. The conclusion deduced from these experiments is the following: If the temperature at the ordinary pressure is sufficiently raised, a large number of elements or carbides can dissolve carbon and subsequently deposit it by simple lowering of the temperature. The carbon set free is always graphite.

C. Action of a High Temperature on Diamond and on Different Varieties of Carbon

After having established this constant formation of graphite in the difficultly fusible metals, it appeared desirable, before going farther, to determine the action of a high temperature on the different varieties of carbon.

Diamond.—In a paper published in the *Annales de Chimie et de Physique* (3e serie, 20) in 1847, Jacquelin showed that diamond is transformed into graphite by heating in the electric arc. It is

easy to show this experiment in the lecture-room in the following manner: By means of a cluster of electric lights two vertical, cylindrical carbons, between which an arc of small intensity is made to play, are projected on a screen. One of the carbons is slightly hollowed and supports a rough or cut diamond of 100 milligrams to 200 milligrams, the image of which under these conditions is clearly shown on the screen. The carbons are then slowly brought together so that the arc plays on the side and slowly heats the diamond so that it does not fly to pieces at the beginning of the experiment. As soon as the temperature is sufficiently high, the diamond becomes incandescent, and soon swells without fusing, becoming covered with black masses of graphite. On examination after the experiment, this graphite appears as hexagonal leaves which can be easily separated and which can be readily converted into graphitic oxide by the action of a mixture of potassium chlorate and nitric acid.

This experiment can be arranged in another manner by placing, in the electric furnace previously described, the diamond enclosed in a small crucible of retort carbon. I have made this experiment with an arc of 300 amperes at 70 volts; the crystal commences to crack into small fragments following the planes of cleavage. Finally, if the temperature is raised, each fragment swells and the transformation into graphite is complete. The irregular or hexagonal leaves are readily separated and on oxidation give a beautiful, yellow-colored, graphitic oxide. Therefore, at the temperature of the arc, even if the arc is not strong,[1] the stable form of carbon is graphite.

In many experiments I had occasion to heat rough or cut diamonds, enclosed in a layer of carbon, to a temperature of about 2000° by means of an oxyhydrogen blowpipe. Under these conditions, diamond is sometimes covered with a black, adherent layer which slowly disappears in the mixture of potassium chlorate and nitric acid, but I only obtained graphite. It is also worthy of note that on burning the Cape diamonds to obtain their ash for analysis, I always observed that at the moment of combustion, the diamond

[1] We have been able to transform diamond into graphite in a small crucible forming the extremity of the positive electrode of an arc of 40 amperes at 30 volts. This arc was produced by a dynamo run by a 4-horse-power gas motor.

was covered by a black coating. This was observed by Lavoisier and since verified by Berthelot.

Sugar Carbon.—Sugar carbon, heated in a closed crucible, was completely converted into graphite and gave no other variety of carbon. The external appearance of the carbon remained the same and under the microscope we could detect no crystallization.

Wood Charcoal.—Wood charcoal, heated under the same conditions, was converted into graphite without a trace of crystallization. Under the microscope, the fibers of the wood always preserved their form. We have given the detail of these experiments in our study of graphite.

Retort Carbon.—The conversion into graphite of the carbon of the electrodes of the electric furnace was shown for the first time by Fizeau and Foucault: *Recherches sur l'intensité de la lumière émise par le charbon dans l'expérience de Davy.*[1]

In these experiments on the preparation of the artificial diamond, mentioned at the beginning of this work, Despretz remarked that his electrodes and small crucibles left a mark on paper and had taken on the appearance of graphite. Berthelot has shown that the crucibles of Despretz, which remained at the University of Paris, had really been transformed into graphite by oxidation of this variety of carbon with potassium chlorate and nitric acid. In our experiments with the electric furnace, we were able to verify this phenomenon.

Lampblack.—Carefully dried lampblack was packed into a small carbon crucible and heated for ten minutes in the electric furnace with a current of 1000 amperes at 70 volts. After the experiment, the density of the carbon was 2.12. It was not attacked by nitric acid, and gave graphitic oxide by the mixture of potassium chlorate and nitric acid. After burning the residue, and after treatment with the oxidizing mixture, then with hydrofluoric acid, no residue remained. Thus, whatever the variety of carbon studied by a sufficient elevation of the temperature, the variety is always brought into the form of graphite. This graphite, as we have previously shown, can be more or less stable, amorphous or crystalline, and can always be converted into graphitic oxide by the mixture of nitric acid and potassium chlorate.

[1] *Ann. chim. phys.*, 3e serie, **2**, 271 (1844).

The experiments were carried out at the temperature of the electric arc, that is to say, at a very high temperature. Certain compounds, iodine-containing bodies in particular, can effect this conversion of carbon into graphite at a lower temperature, as Berthelot has shown. But these are reactions like that of iodine or ordinary phosphorus, which cause a polymerization to be produced without modifying the general character of the phenomena.

From these experiments we conclude that graphite is a variety of carbon, stable at high temperature and at the ordinary pressure.

Study of the Vapor of Carbon.—Before going further, it appeared necessary to investigate the vapor of strongly heated graphite. Hitherto the formation of the vapor of carbon has been determined in the electric furnace either by means of the spectroscope, or by the synthesis of acetylene by Berthelot. It is possible to show the existence of this vaporization outside of the arc in the following manner: If a carbon tube, 2 cm. in diameter, is placed in an electric furnace of lime, heated with an arc of 2000 amperes at 80 volts, the interior of the tube becomes rapidly filled with a light black coating produced by the condensation of the vapor of carbon. It is possible to render this vapor visible by placing crystalline silicon in a boat in the center of the heated carbon tube. The silicon is seen to melt, then begin to boil and the vapor rising, little by little, meets the vapor of carbon which descends from the top of the tube under the action of the heat of the arc. Between the boat and the tube is formed a network of fine needles of carbon silicide. This crystalline and transparent compound is formed by the direct union of the two vapors.

At the high temperature produced in the electric furnace, it is possible to vaporize carbon outside of the arc. We thought it would be interesting to investigate how this vapor is produced. In general, a body passes from the solid to the liquid state, then, after a sufficient elevation of the temperature, it passes into the gaseous condition. Does carbon act in a similar manner or is it an exception to the general rule? The following experiments should answer the question.

In the electric furnace, heated by an arc of 1200 amperes at 80 volts, we placed a small crucible of pure carbon in which a heavy cover was pressed deeply. This crucible was placed on a disk of

carbon supported by a layer of pressed magnesia and was heated for ten minutes. The heat was sufficiently intense to volatilize several hundred grams of lime and magnesia. On cooling, the cover which was resting in place did not adhere to the crucible; the entire mass was converted into graphite but the two surfaces were not united. When a boat of carbon was placed in a tube of the same material and the tube heated either above or below by means of a powerful arc or by a number of arcs, the boat was never fused into the tube.

By the action of an arc of 1000 amperes at 80 volts in our electric furnace for tubes, it frequently happened that the upper part of the tube, which was more exposed to the heat of the arc, became perforated, while on cooling the edges of the opening showed no traces of fusion.[1]

With an arc of 1000 amperes at 70 volts, we heated sugar carbon in a closed crucible. The sugar carbon retained its form and still showed the pores through which the hydrocarbons were evolved during preparation. It was completely transformed into graphite, but the pulverulent mass examined with the low power of the microscope showed no sign of fusion.

On heating, under similar conditions, graphite, wood charcoal, or retort carbon purified by chlorine, at the end of the experiment not only was graphite found, but each variety of carbon preserved its form and showed no sign of fusion or sintering. On examining the electrodes which were of as pure carbon as possible, and which were used in these experiments, it was observed that the points were rounded and completely converted into graphite, but they showed no trace of fused material. With a current of 2200 amperes at 70 volts, the transformation of electrodes of 0.05 meter in diameter extended for a length of 15 cm.

Analysis of the graphite taken from the ends of the electrodes showed:

[1] Thanks to the kindness of Meyer, director of the Edison Society, we were able, durthe summer of 1894, to pursue these experiments on the volatilization of carbon, by means of a 300-horse-power dynamo. Under these conditions we had, in our electric furnace, an arc of about 2200 amperes, at 70 to 80 volts, the energy used in the electric furnace being 200 horse-power. There was thus obtained an intense heat, and in the cavity of the furnace, the farthest points of the arc were exactly at the temperature of the volatilization of lime. The cavity of the furnace enlarged more and more according to the length of the experiment.

Carbon	99.63
Hydrogen	0.03
Ash	0.39

Before the experiment, the quantity of ash was about 1 per cent. Since all of the mineral matter was more volatile than the carbon, the electrode was slowly purified by volatilization.

The end of the positive electrode was formed of a cylinder of carbon fitted tightly, and, after the experiment, this cylinder which was in the hottest part of the arc was distorted but was not fused to the electrode. It is well to mention that this was even more the case if the carbon used contained, as impurities, metallic oxides, as silicon, or boric acid.

We have already shown that boric acid in this case gives a definite crystalline boride of carbon, having the formula B_6C. This boride of carbon can unite with an excess of carbon and form a body having a fused appearance, and more or less rounded. These rounded bodies were sometimes very hard but were not formed of pure carbon. A very small quantity of metallic impurities can give fused or crystalline carbides, many of which I have described. It is thus necessary in these experiments, to use as pure carbon as possible.

According to these experiments, carbon passes from a solid to a gaseous state without becoming liquid. It remained to study the variety of carbon produced by the condensation of this vapor. We collected the vapor of carbon in three different ways:

1. By Distillation.—Carbon vapor, condensed in a tube of carbon, such as we have previously described, gives a black deposit entirely formed of graphite.

2. By Condensation on a Cold Body.—When we placed a copper tube, through which a current of cold water[1] passes, in our electric furnace, we collected on its surface a black deposit, which was treated in the cold with dilute hydrochloric acid to remove the lime and calcium carbide. This deposit contained small globules of silica and other impurities, but was composed mainly of an impalpable powder, which swam on water, had a gray color under

[1] H. Moissan: "Étude de quelques phénomènes nouveaux de fusion et de volatilisation produits an moyen de la chaleur de l'arc électrique," *Compt. rend.*, **116**, 1429, June 12. 1893.

the microscope, and which possessed all of the characteristics of amorphous graphite.[1]

3. By Condensation of a Cold Surface.—When the electric arc is allowed to play in a lime furnace, in order to avoid the carbon dioxide which transforms the vapor of carbon into carbon monoxide, there is formed, especially on the negative pole, a spongy form of carbon which appears from the vaporization of carbon in the arc itself. When the electric furnace of lime has been in operation for fifteen to twenty minutes, it is frequently observed that this spongy form of carbon is deposited on the two poles. In some experiments where a current of a cold, inert gas was passed through the furnace, we found filaments of carbon uniting the two poles following the rapid fall of potential.

This carbon, whose surface was more or less rounded, when examined under the microscope, showed no fused appearance. Its density was 2.10. On analysis, it gave 99.61 to 99.90 per cent. of carbon and contained only a very small quantity of ash.

Its quantitative analysis was:

Carbon	99.61	99.84	99.90
Hydrogen	0.018	0.03	0.031
Ash	0.023	0.018	0.017

It was, consequently, pure carbon produced by distillation. It showed all of the characteristics of graphite and only burned in oxygen at a high temperature, and could be burned only in a porcelain tube. Deslandres has studied the spectra given by this carbon and has found that it contains fewer lines than the corresponding spectra published by Liveing and Dewar, Hartley and Adeney, Eder and Valenta.[2] Without exception, all of these condensations of carbon vapor gave graphite.

When these experiments were conducted, we thought of verifying them by a small and simple piece of apparatus—the incandescent lamp. To-day every one knows the construction of this piece of apparatus. A carbon filament is united by means of an electrolytic copper deposit to the ends of two small platinum wires. This

[1] If the material which is condensed on the under part of the copper tube is collected, that is on the side toward the electric arc, small crystals of graphite are found which come from the liquid drops of calcium carbide thrown on all sides in the lengthy experiment.

[2] Deslandres: "Étude spetrale des charbons du four électrique," *Compt. rend.*, 120, 25, June 10, 1895.

filament is enclosed in a glass bulb, which has been exhausted by means of a mercury pump. According to the time of use of varying between 500 and 900 hours, a light veil is formed on the glass. This deposit increases and frequently renders the lamp useless. On the other hand, under the action of too strong a current, the filament burns at a point and quickly gives the same deposit, which is uniformly formed on the interior of the bulb. A trace of silica or a calcium salt accidentally deposited on the carbon filament can give carbon silicide or fusible and volatile calcium carbide, which causes a shrinking in diameter of the filament. At this point the resistance increases, and the current raises the temperature; from that time, the carbon is volatilized and the filament soon breaks.

If the black deposit which is found inside the glass bulb is collected in a vessel filled with water, on examining with the microscope, there are observed small crystals of carbon silicide having the characteristic form, these crystal masses resembling the silica obtained by Marsden in fused silver and small, more or less united aggregates of black color. This deposit with a high power does not show a trace of crystallization. In our experiment a small particle swam on the liquid, which under the microscope showed brown color. The contents of the lamp were treated with a mixture of nitric acid and potassium chlorate, but the black material was not immediately destroyed. This mixture was maintained for twelve hours at a temperature of 60°; after washing and decanting, the light residue obtained was examined with the microscope, and showed distinct crystals and small particles of graphitic oxide. The cover glass was raised, the liquid evaporated and the residue on the same glass slide heated to dull redness.

Another microscopic examination was made and showed that all of the crystals and yellow or green particles had burned, and were replaced by a black, flocculent deposit much more voluminous. This deposit disappeared in turn by burning at a low red heat in air. We conclude from this experiment that the veil formed on the incandescent lamps is composed mainly of graphite.[1]

If, on the other hand, a microscopic examination is made of the ends of filament which are broken in the incandescent lamp, it is

[1] The small particle which swam on the liquid was also graphite, which after burning left a pyrographitic oxide which burned easily.

seen that the points of the filaments show no fusion and the ends bristle with small crystals of graphite.[1] From these experiments we can conclude that in vacuum, as well as at the ordinary pressure, carbon passes from the solid to the gaseous state without taking on the liquid form. From this point of view it can be compared with arsenic. When gaseous carbon resumes the solid condition it always gives graphite.

D. Experiments under Pressure

The preceding experiments on the vaporization of carbon, the work on the action of a high temperature on the different varieties of carbon, as well as the constant formation of graphite in fused metals, gave a new direction to our researches.

The geological studies made on the different rocks in which crystalline carbon is found, establish indisputably that the diamond is not a vein mineral.[2] No crystal has been found on a rock which serves as its support. Sometimes diamonds are found in alluvial sands, sometimes in soft conglomerates, or in a serpentine breccia. Moreover, I never found in the mines of the Cape two broken pieces of the same fragment lying side by side. The mass which contains the mines has been thrown out from below and formed together.

The diamond preexisted in this serpentine breccia, since, on the contrary, it would be necessary to assume that the 80 mineral species, found disseminated in this rock, were formed under same conditions. Is it possible that calcite, the zeolites, topaz, garnet, zircon, and titaniferous iron can be formed in the same substance and under similar conditions? The diamond must then come from the deeper layers of the earth where it must originate, where pressure plays a part in its formation. Moreover, it seems to us that proofs are plenty to establish the importance of pressure in the production of the diamond. The depths of the mines that to-day are more than 500 meters is a fact which seems to support this theory.

Moule has shown that granite is found in the vertical shafts of the Cape. Now, granite is a rock which, according to the

[1] The graphite forming the filament is more difficultly converted into graphitic oxide than the deposit in the interior of the lamp.

[2] Numerous works treat on this question, but I would like to call attention to the work of Boutan having the title of "Le Diamant" in the "Encyclopédie Chimique" by Frémey.

views of all geologists, was formed under pressure. It, then, like the diamond, came from great depths. Certain diamonds show striations that, according to Daubree, can only be attributed to the rubbing of one on the other in coming from the lower to the upper strata.

It sometimes happens that the diamonds taken from the blue ground of the Cape are frequently cleaved or cracked open. Cannot this phenomenon be considered as indicating an unstable physical state due to a strong pressure which has acted at the time of formation of the diamond? None of the diamonds in all that I found show clearly a point attached to any rock whatever. It appears as though the diamond had formed in a liquid or pasty mass; consequently it is necessary to know the solvent which has been used.

According to the known properties of carbon and according to the experiments described in this work, it is mainly the metals which dissolve carbon, and best of all, iron. When it is remembered that the blue ground of the Cape contains, as I have shown, perfectly crystallized graphite, and that well-crystallized graphite is formed most readily in fused metals and not by volatilization, there is introduced the crystallization of carbon in fused iron under pressure.

I would add that the study of the ash of the diamond, in which iron is always found, leads to the same conclusion. It can be said that this metal is found widely disseminated in nature; but the quantities which are found in certain borts and in some black diamonds appear too large to be due to a distribution compared to that of manganese and boric acid. From this point of view it is somewhat remarkable that among all the minerals which are found in a cubic meter of the blue ground, the most abundant by far is titaniferous iron, as Stanislas Meunier has shown.

Finally, a last proof was afforded by the iron of Canon Diablo, where, in a metallic mass surrounded by amorphous carbon in clearly compressed layers, two small transparent diamonds having a rough and wrinkled surface were found. Here nature seems to have been caught in the act. This carbon must have crystallized under the action of a strong pressure; the iron was in a liquid state and owing to the rapid cooling, due to some cause, there was

a violent contraction of the mass and the carbon passed from a density of 2 to 3.5, giving the diamond.

Such are the ideas, true or false, which brought about the change in the direction of my investigations on the diamond and caused the intervention of pressure. I do not know if this theory will stand the tests of my successors, but it is to it that I owe the experiments which I will describe and what have brought about the preparation of the artificial diamond in microscopic crystals.

Detail of the Experiments.—In order to make the experiments, I utilized the pressure produced by the increase of volume which a fused mass undergoes at the moment of passing from a liquid to a solid state. It is known that solid cast iron has a less density than liquid. It is a fact known in industry that pig iron floats on the surface of a bath of the fused metal.

Cast iron, like water, increases in volume at the moment of solidification. We began these studies by heating in an oxyhydrogen blowpipe, a small quantity of iron in a carbon crucible, then immersing the whole in cold water.

Since the first experiments gave only doubtful results, we thought it was necessary to saturate the iron with carbon at a higher temperature. To obtain this result we used the electric furnace. At the high temperature, furnished by this apparatus, iron dissolves a large quantity of carbon, which is subsequently deposited as graphite when the iron again solidifies. This experiment was carried out in the following manner: 200 grams of soft Swedish iron cut into cylinders, 1 cm. to 2 cm. in length and about 1 cm. in diameter, were placed in a carbon crucible and completely covered with sugar carbon. Since, at the beginning of this work, we gave the arrangement of the electric furnace, it is not at present repeated. It was heated from three to six minutes with a current of 35 amperes at 60 volts. The cover of the furnace was raised by the hand wrapped with a cloth, the edge of the crucible was grasped with a pair of iron tongs, and was plunged into a vessel filled with cold water. The crucible and contents remained at red heat for several minutes, with evolution of bubbles of gas which burst at the surface without taking

fire. The temperature fell rapidly, the light faded and the experiment was ended (Fig. 24).

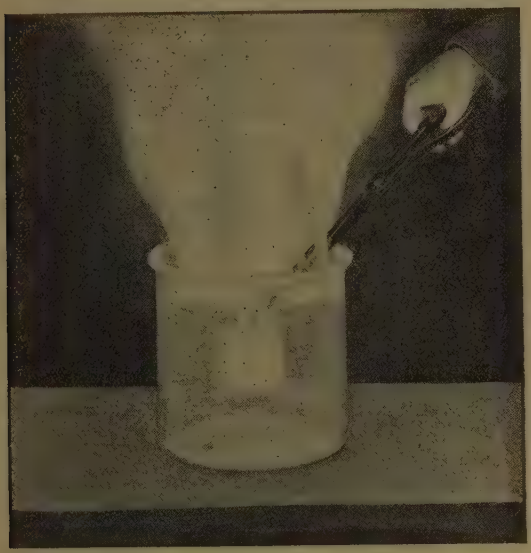

Fig. 24.

It was not without great care that we made this experiment the first time, for I wondered if there would not be an explosion when a crucible of molten iron, having a temperature of 3000°, was introduced into water. The experiment is actually without danger due to the great heat. We were able to prepare 250 to 300 ingots of iron by sudden cooling and we never had an accident. With other metals, bismuth in particular, this was not always the case.

The metallic ingot was treated with boiling hydrochloric acid until no iron remained. There then remained three kinds of carbon: A small quantity of graphite when the cooling was rapid; a brown colored carbon in very thin, distorted layers apparently having been submitted to strong pressure (we found the same variety in the specimens of iron from Canon Diablo); finally, a very small quantity of a somewhat denser carbon was formed, which we endeavored to separate.

It was repeatedly treated with aqua regia, then alternately with boiling sulphuric and hydrofluoric acids. The residue was introduced into sulphuric acid and heated to 200°, while small quantities of powdered potassium nitrate were added. All of the amorphous carbon was destroyed. The heavier portion, examined with the microscope, contained only very little graphite and the different varieties of carbon. It was treated six or eight times with potassium chlorate and fuming nitric acid which we prepared as free from water as possible. After a final treatment with boiling hydrofluoric acid, then after decantation with boiling sulphuric acid, to destroy the fluorides formed, it was washed, the residue dried and the heavier particles separated by means of bromoform.

After the first separation with bromoform, the small residue that sank to the bottom of the liquid was washed with ether and introduced into a small tube containing methylene iodide. Some small, transparent particles sank to the bottom, and black fragments swam on the surface. Both were collected and separately introduced into a conical wine-glass with a large excess of distilled water.

It was taken up with a pipette (see technique of the investigations), brought on a glass slide, covered with a slip and examined with the microscope. The opaque particles had a rough appearance, a gray-black color, similar to the specimens of black diamond. Their density varied between 3 and 3.5, since some sank in methylene iodide and others in bromoform. Some had a less roughened surface and a deeper black; one showed curved

Fig. 25. Synthetic black diamonds, magnified 100 diameters.

edges. Others had well-terminated angles (Fig. 25) and which at first sight appeared to be cubical.

In order to ascertain if these fragments scratched corundum, a ruby having a polished face was fastened with a little Golaz cement to a piece of thick looking-glass. With a fine point of hard wood, moistened with water, the small, black fragments were

touched, then rubbed strongly on the surface of the ruby. Care was previously taken to see with a low power of the microscope that this surface was well polished. The point of wood was drawn across the ruby perpendicular to the striations of polishing. On again observing with the microscope, if the particles dragged along by the pieces of wood were sufficiently hard, lines were seen more or less deep on the horizontal surface of the ruby. After each trial the surface of the ruby was freshly polished. This proceeding enabled us to determine the hardness of the finest powders. (By making the surface of the ruby reflecting, the slightest striation could be found.) The black powder, of which we have spoken, readily scratched the ruby.

It remained to burn it in oxygen. We made a small platinum boat with a hollow cover in which were stamped four small cups and which was highly polished (Fig. 26). The small black frag-

Fig. 26. Platinum boat.

ments were taken from the wine-glass filled with water, at whose bottom they were deposited by means of a pipette formed out of a thin tube. Then, on placing the point of the pipette in the cup, the fragments sank, due to their density, and rested with some water on the surface of the platinum. The boat was placed in an air-bath to evaporate the water. The small cup which contained the black fragments were placed under the microscope and the outlines were drawn by means of a camera lucida. The boat was placed in a small platinum apparatus (Fig. 27) constructed of a

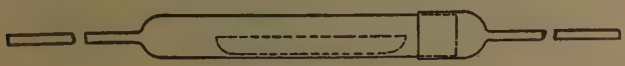

Fig. 27.

tube closed by a piece joined on and closely fitting, while a current of oxygen was passed through it. The apparatus was heated in the central portion, which contained the boat, by a blast-lamp whose temperature was about 1200°. The tube was heated twenty to thirty minutes, allowed to cool, again placed in the field of the

microscope in the same manner as before. The contents of the platinum cup were drawn by means of the camera lucida, which was easy to do, as the bright bottom formed a mirror. On comparing the two drawings it could be determined if the particles had disappeared and if in their place an ash remained.

The platinum tube of which we have spoken could be replaced by a tube of Berlin porcelain, 0.30 meter long and to which glass outlet tubes were attached by Golaz cement. At the end of the apparatus a small apparatus containing baryta water was placed and this immediately became turbid from the carbonic acid. A similar apparatus was placed in front of the combustion tube and was separated from the latter by a tube of fused potash to show if the oxygen prepared by us contained a similar quantity of carbon dioxide. A trace of carbon could be readily detected by this proceeding as I assured myself by preliminary experiments.

The black diamonds, having a density of 3 to 3.5 obtained from our iron fusions, burned in oxygen and gave carbon dioxide, leaving a very light residue of yellow ash, at the place it occupied in the little platinum cup. The transparent fragments had an oily appearance, they allowed light to pass through and possessed some parallel striations and sometimes triangular impressions. These fragments were frequently surrounded by a cover of black carbon; this was discovered on treating with potassium chlorate, which was frequently repeated ten times.

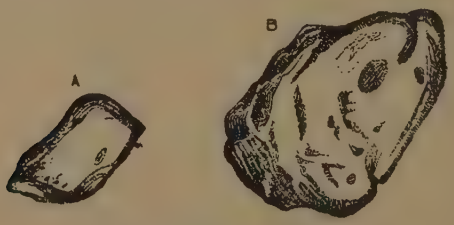

Fig. 28. Magnified 100 diameters.

Some of these diamonds had a rounded surface (Fig. 28, B); others appeared broken into small pieces (Fig. 28, A). One of the fragments, A, was colored light yellow as was also the cube B in Fig. 29. Others appeared in the form of cubes (Fig. 29, B) or possessed an irregular form (Fig. 29, A and C). The density of

all was about 3.5, since they sank in methylene iodide; they scratched the ruby and burned in oxygen, leaving no ash, or only a little light yellow ash, and formed carbon dioxide.

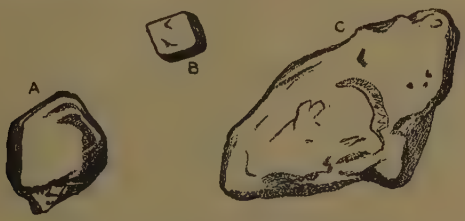

Fig. 29 Synthetic transparent diamonds.

Since the product of the first experiment was so small, we were able to collect only a few milligrams of the transparent crystals which were necessary in order to weigh the carbon dioxide formed in the combustion; moreover, some of the fusions gave nothing as the pressure was not great enough. Sometimes it happened that the metallic crust, formed by the sudden cooling, was broken and the still liquid metallic interior was thrown to the surface. On the other hand, the gases evolved formed geodes in the metal and prevented the pressure being regular. In these cases, which frequently occurred after the treatments with potassium chlorate and hydrofluoric acid, nothing remained when examined under the microscope.

In order that the preparation should better succeed, we endeavored to enclose a fusion in soft iron. The experiment was conducted as follows:

Sugar carbon was strongly compressed in a soft iron cylinder closed by a screw stopper of the same metal (Fig. 30). This

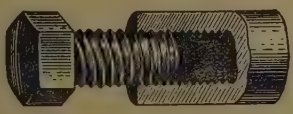

Fig. 30.

cylinder was 0.04 meter high and 0.07 meter internal diameter. Its thickness was 8 to 10 mm. From 50 to 200 grams of soft iron were melted in the electric furnace, an operation which takes only a few minutes; then the cylinder containing the carbon was

quickly introduced into the liquid bath. The crucible was immediately removed from the furnace and plunged into a pail of water. A rapid formation of a layer of solid iron was obtained, and when the crust was at dull redness it was removed and the cooling completed in air.

When the fusion thus formed was broken, a layer of cast iron was found on the outside, then metal less carbonized, and in the center, a portion rich in carbon, in which were found small diamonds. The quantity of black diamond formed appeared greater than in the preceding method. The yield was a little greater, though always very small. A large number of the fusions were of no value on account of the breaking of the external layer or on account of the formation of geodes. The subsequent treatment of the fusions was made according to the methods previously described.

We obtained black diamonds (Fig. 31) and as well transparent

Fig. 31. Black diamonds from the cylinder, magnified 80 diameters.

diamonds. One of the transparent diamonds (Fig. 32) measured 0.38 mm. or about 0.4 mm. in its longest direction. Its appearance was characteristic; it sank in methylene iodide, and disappeared by burning in the small platinum boat at 900° with the formation of carbon dioxide. On carefully withdrawing the boat from the tube in which the combustion was made, in the place of the small fragment, there was found a trace of ash, scarcely visible under the microscope, which preserved the original shape and which had a yellow-gray color.

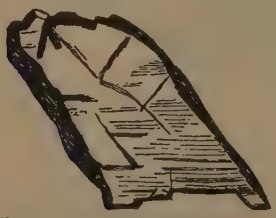

Fig. 32. Transparent diamond from the cylinder.

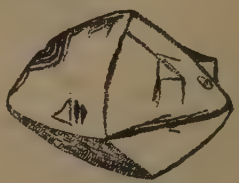

Fig. 33. Magnified 100 diameters.

A beautiful, clear and well-crystallized diamond (Fig. 33) made in another experiment burned in oxygen without leaving any ash. In general, when the iron used in these experiments was free from silicon and when the crucible did not contain aluminum, the black or transparent particles left no ash when burned in oxygen.

Experiments in Iron Filings.—It appeared to us that the rapidity of the cooling had an important influence on the formation of crystalline carbon. On cooling the crucible in water, the heating completely prevented contact between the red-hot iron and the liquid. At the beginning, the cooling was mainly by radiation. In order to more quickly lower the temperature we attempted to cool the liquid fusion by conduction. To this end, 200 grams of iron, saturated with carbon in the electric furnace, were poured in a cavity made in the center of a mass of iron filings and then completely covered with the filings. The fusion was surrounded by fused iron and the whole rapidly cooled, due to the conductivity of the filings. After action of the acids, the treatment with potassium chlorate and nitric acid, and the action of hydrofluoric acid, then with boiling sulphuric acid, there remained small diamonds having a rounded form and rarely showing a crystalline appearance and almost always enclosing small black points which are called spotted diamonds in jewelry.[1]

These spotted diamonds had a density of 3.5, scratched the ruby and burned readily in oxygen, giving carbon dioxide. In

1 In Brazil, as well as at the Cape, natural, transparent diamonds are found which contain inclusions. These inclusions are of different kinds but the most numerous are black and, when abundant, give the variety of crystalline carbon having a greasy appearance, which is known under the name of *black diamond.*

It is possible to show that these black inclusions are due to a variety of carbon differing from diamond; a black diamond of 2.2365 grams, showing some small, transparent regions, was wrapped in a piece of linen cloth, placed on an anvil, and broken with a hammer. It cleaved at the first blow, giving a distinct octahedral termination. We reduced the whole to a fine powder in the mortar, and this powder, examined under the microscope, was formed of fragments containing many spots.

About a centigram of this powder was then heated in a tube of Bohemian glass, in a current of oxygen, to a temperature 200° below the combustion point of the diamond. The experiment lasted for half an hour. A slight evolution of carbon dioxide was shown by baryta water. On cooling, the diamond has lost its gray tint; it became white and under the microscope no spots could be found. The black material which was enclosed in this diamond burned then in oxygen with the formation of carbon dioxide and the diamond became transparent.

The experiment only succeeded when the black diamond was reduced to a fine powder. A splinter of black diamond heated under similar conditions was not decolorized. Possibly the experiment would succeed if the diamond were carefully heated in compressed oxygen.

this experiment the pressure appears to have been less and the conversion of carbon into diamond less complete; the yield, moreover, is always very small. The experiment of cooling in iron filings was repeated a large number of times (about forty times). When the fusion had been regularly formed and when it contained no cavities, the result was always the same. The form of the spots was variable, sometimes forming small, black spots distributed by chance, sometimes forming local regions (Fig. 34).

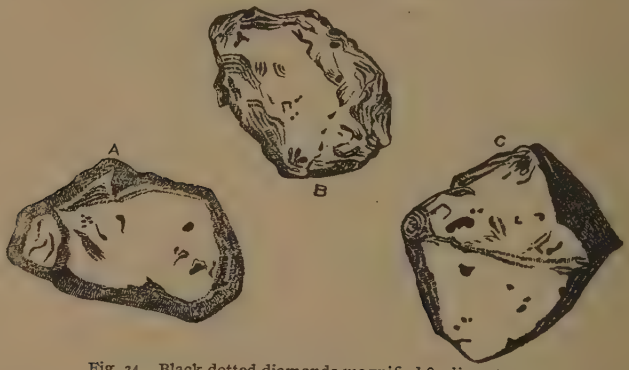

Fig. 34. Black dotted diamonds magnified 80 diameters.

We regard this formation of diamonds with spots as very important, since it gives results similar to those found in nature. Moreover, from their peculiar appearance, it was possible to recognize at once that the fragments were diamonds. In fact, it sometimes occurred that small, transparent grains were obtained whose density was greater than methylene iodide and which resisted all of the treatments with the acids and potassium chlorate, and which were not formed of carbon. These particles never showed definite angles, striations, or triangular impressions; they were rounded and did not burn in oxygen. After combustion they were found in the platinum cups, their form was not changed, frequently their surface was only slightly corroded. This substance was formed especially with irons rich in silicon, or when the electrode contained a considerable quantity of silica or alumina; we accordingly returned to the quantitative analysis of the synthetic diamond.

Experiments Made in Melted Lead.—The formation of

diamonds with spots brought about the investigation of more rapid cooling by conduction. We thought of cooling the liquid iron which was saturated with carbon, by plunging it into a bath of melted tin. The experiment did not give good results because the strongly heated iron readily united with the tin; in the middle of the liquid there were formed long filaments of an alloy of iron and tin, so that we had no coherent mass.

Moreover, when we plunged the crucible, filled with iron at 3000°, into the bath of melted tin, kept at its melting-point, the combination of the iron and the tin evolved heat, and the entire mass was raised to a temperature too high for our experiment to succeed.

Since tin gave only negative results, it was replaced by melted lead, kept as near as possible to its melting-point; that is to say, about 325°. The crucible containing the fusion was rapidly introduced to the bottom of a lead-bath about 0.10 meter deep. The fused mass being lighter than the melted lead, it detached from the crucible in masses which tended to assume the form of spheres and which rose through the liquid lead. When iron is saturated with carbon in the electric furnace it is so pasty that it is possible to invert the crucible without anything flowing out. As soon as the temperature falls the metal again becomes liquid, and at the same time graphite separates. The smallest spheres, those only 0.01 meter to 0.02 meter in diameter, were solid and sufficiently cooled on arriving at the surface of the bath. On the other hand, when it reached the upper portion of the lead, while still liquid, the lead burned in the air with evolution of copious fumes of litharge, and sometimes projection of the oxide or incandescent metal. A little later all of the metallic globules which floated on the melted lead were removed, and the lead with which they were covered was removed by nitric acid. They were then submitted to the treatment previously given for the other metallic fusions.

Under these conditions, the yield which, on the whole, was always very small, was a little better. What surprised us at first was the clearness of the transparent diamonds thus obtained: we obtained none of the diamonds with spots, and the surface of some showed distinct crystallization. We found many parallel striations and small impressions of cubes similar to those which are sometimes found on natural diamonds.

One of these transparent diamonds (Fig. 35) whose diameter

Fig. 35. Diamond by cooling in lead.

attained 0.57 mm., showed the form of a triangle with rounded angles. It was perfectly clear; on one place, on the right, it showed a small cavity, and its surface was covered with impressions having the appearance of small cubes. Three months after its preparation, this diamond, which was preserved between two plates of glass, cleaved into two different parts. For some time we could observe the increase of these small cracks and at the end of three weeks the diamond was found to be broken in many parts. This accident was also produced on another specimen which was found to be broken into small parts, having been preserved between glass plates.

This formation of diamonds which break several months after their preparation seems significant. It is known that some diamonds, taken from the mines of the Cape, show the same phenomenon. It seems that these accidents to the microscopic fragments which we have obtained and to the diamonds of the Cape, can be attributed to the strong pressure to which both have been subjected at the time of their formation.

The specimens of diamond, prepared by this method of cooling in melted lead, were very curious when examined from the standpoint of their formation. Frequently their surface was bright and smooth, sometimes it was rough and hollowed out, having the peculiar appearance which is often found on the natural diamonds. These crystals had a sharp outline and always possessed the greasy appearance that is peculiar to the diamond. When a ray of light penetrates them they become illuminated and appear to absorb the light. Some appeared in cubes or in octahedrons with rounded faces. Bouchardat, professor of mineralogy in the *École supérieure de Pharmacie,* kindly examined these crystals as to their form, and found one among others which

clearly possessed the form of a trapezohedron with twelve faces, that is, it was a hemihedral form of the isometric system.

Examined in convergent polarized light, sometimes these crystals (Figs. 35 and 36) gave no color phenomena (this was gen-

Fig. 36. Diamond by cooling in lead magnified 100 diameters.

Fig. 37. Diamond crystallized in cubic form magnified 100 diameters.

erally the case); sometimes they took on a faint color (Fig. 37). We had many occasions to study the crystals of natural diamonds which showed a much deeper coloration. It seems that this coloration can be readily explained by the pressure necessary for the formation of the crystals.

We will describe some of them. The one shown in Fig. 37, whose greatest length measured 0.40 mm., was a perfectly transparent stone which throughout showed the smallest details in the lower portion. It was an aggregation of crystals as broad as it was long and showed numerous four-sided impressions. It was formed of superimposed layers with irregular crystallization. On the sides, numerous parallel striations could be distinguished. The diamond, shown in Fig. 38, had the appearance of a drop which

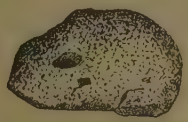

Fig. 38. Diamond in form of drop magnified 80 diameters.

was suddenly solidified. Its surface was rough and its appearance was similar to some diamonds from Brazil. Its appearance is entirely characteristic.

Experiments Made by Granulating Fused Metals.—In another series of experiments we endeavored to diminish the quantity of the melted iron and to cool it much more rapidly.

The idea was to bring the fused liquid into the form of a sphere, and then exert a great pressure on it. Such a result can be obtained on a small quantity of substance, by allowing liquid iron, saturated with carbon by means of the electric furnace, to fall from some height, and suddenly cooling it in a mercury-bath. We used an electric furnace of Courson stone, similar to those which we daily used, but of which the bottom carried a cylindrical opening 6 cm. in diameter. The electrodes which carried the current were 5 cm. in diameter; the positive was hollowed and contained along its axis a cylindrical canal, 18 mm. in diameter, in which a bar of iron could easily be moved backward and forward at will.

This furnace (Fig. 39) was arranged on two supports, while

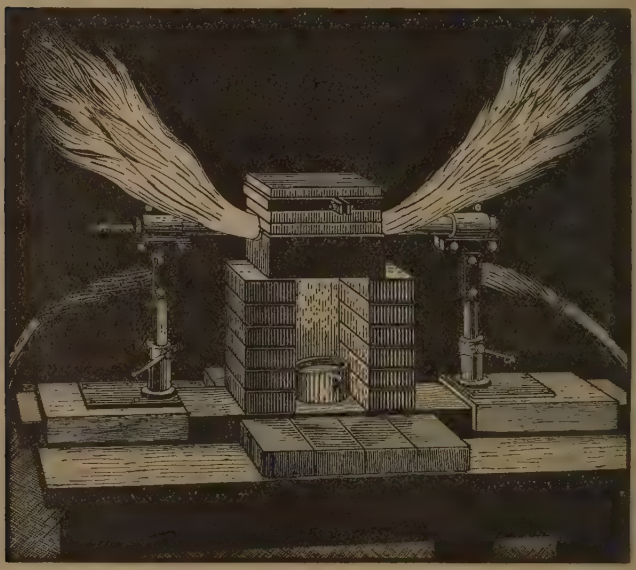

Fig. 39.

underneath was an iron pan containing 10 cm. of mercury covered

by a layer of water twice as thick. At the beginning the arc was made to play with a current of 1000 amperes at 60 volts. When the furnace became regular and the lime commenced to distil, which took at most two or three minutes, the iron bar was slowly pushed forward; the metal approaching the arc, rapidly fused, became saturated with carbon, then fell in the form of regular spheres. These incandescent spheres passed through the layer of water and in consequence of their acquired speed sank to the bottom of the mercury, where they cooled by conduction.

When the experiment is once in progress it is easily regulated, and it is possible in a short time to granulate many kilos of melted iron. When this granulated mass which swam on the surface of the mercury was collected, a large number of spheres or flattened ellipsoids were found to be regularly formed and perfectly homogeneous. At most they measured 0.01 meter in diameter, sometimes only 4 to 5 mm. They were preserved for the usual treatment with acids, as previously indicated. The other irregular grains, which were porous or which contained geodes and easily crushed under a hammer, were not treated with the acids. We found in the first experiments that they contained no carbon of high density, and after the usual treatment left no residue under the microscope. All of the fusion was sufficiently saturated with carbon, since it contained graphite, which could be seen in the geodes of the grains of poor quality.

The regular formed spheres gave black and transparent diamonds. The latter were in very small crystals, which was not

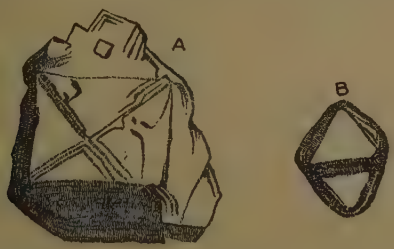

Fig. 40. Diamonds from granulation of iron magnified 100 diameters.

surprising. Some of the crystals showed a remarkable regularity; for example, an octahedron (Fig. 40, A and B) measuring 0.01€

mm. in its greatest length, sank in methylene iodide and burned on the platinum boat, leaving no ash. These little crystals scratched the ruby and possessed the brilliancy and appearance of the diamond.

Thanks to Guichard, engineer of the Société Edison, we were able to make the same experiment in another form. The electric furnace was arranged above a pit 32 meters deep, at the bottom of which was placed an iron pail containing water and mercury. As soon as the furnace had attained a constant temperature we shoved the iron bar in the axis of the positive electrode, being careful to fuse a sufficiently large quantity of metal in order that the drops formed would be large in diameter. The spheres of fused iron which attained a diameter of 0.02 to 0.03 meter fell vertically, giving now and then a spark and disappearing without burning in the water placed at the bottom of the pit. From the standpoint of production of the diamond this experiment was very poor, as the depth of the mercury was insufficient for such a rapid fall and the fused metal was scattered into fragments of indefinite shape.

Two facts were observed in this experiment: When one of these spheres touched the edge of the tube in whose center the metallic pail was placed, or when it encountered the ground, it burst into flame, breaking into sparkling globules, making a sound like a gunshot. This sphere of metal appeared saturated with gas and burst like a ball of fire. The second fact which struck us was the following: At the moment when the ball of metal left the electric furnace, it was brightly glowing, but in its rapid fall traveled only 0.50 meter before the bright light was much diminished. A camera on the bottom of the pit enabled us to observe the spheres at the moment when they came in contact with the water, and according to their color, we can say that their temperatures had fallen considerably.

Experiments Made in Metallic Blocks.—In this work we replaced the mercury by a metallic block. An iron cylinder 0.18 meter long and 0.14 meter wide was turned on the lathe. A cylindrical hole was bored along its axis 3 cm. in diameter and 0.12 meter deep, in which a cylinder of the same metal could slide with gentle friction. This apparatus was placed in a bucket of

cold water. Four hundred grams of iron, saturated with carbon, were fused in the electric furnace and the liquid was cooled in the metallic block which was quickly closed by means of the iron cylinder. In these experiments, the cooling was very rapid. The metal which formed the block was removed on the lathe and the fused mass found inside was submitted to the treatment previously described.

This experiment gave the best results; the yield without being high was more than from the granulated metal. The diamond was accompanied by a graphite in compact crystals having a density of 2.35. Some particles of the diamond were well-crystallized and perfectly transparent, while others contained spots. In order to still further increase the rapidity of cooling we repeated the same experiment in a copper block of the same dimensions. The yield in weight was not higher, but the diamonds were quite transparent, and the number of diamonds with spots was less. They were not accompanied by the dense fragments which were transparent and which would not burn.

Sheath of Fire.—The phenomenon of the sheath of fire was discovered by Fizeau and Foucault;[1] it was later studied by Plante, then by Violle and Chassagny,[2] and finally by Hoho and Lagrange who sought to apply it industrially.[3]

This phenomenon, which is produced when a strong current is passed through a liquid conductor, causing the metal of an electrode to fuse, enables the metal of an electrode to be raised to its fusion-point. We made this experiment with a tube of cast iron containing in its axis a cylinder of carbon and collected the drops of metallic liquid in a solution of sodium carbonate which served as the electrolyte.

The drops thus obtained were always irregular in form and incompletely saturated with carbon. They contained no diamonds.

Attempt at Solution of Carbon in Bismuth.—It is known that bismuth possesses, to a high degree, the property of increasing in volume on passing from a liquid to a solid state. We investigated the solubility of carbon in this metal. The experiment was made

[1] Fizeau and Foucault: "Recherches sur l'intensité de la lumière émise par le charbon dans l'expérience de Davy," *Ann. chim. phys.*, 3 série, II, 383 (1844).

[2] Violle et Chassagny: Société de Physique, 1889, and *Compt. rend.*, February, 1880.

[3] Hoho and Lagrange, March 13, 1893.

by heating bismuth in a carbon boat, placed in a tube of the same substance in an electric furnace. The current employed was 350 amperes at 60 volts. The experiment was made very short on account of the ready volatilization of the metal. On cooling the mass which was not volatilized, bismuth remained which contained neither amorphous carbon nor graphite. Bismuth was then heated in the presence of sugar carbon in a carbon crucible with a current of 350 amperes at 60 volts. When the mass was red-hot it was plunged into water, when a violent explosion took place with projection of the water and all of the metal; the latter was pulverized into very small fragments. The experiment was repeated with similar results.

Sudden Cooling of Silver.—Silver, when saturated with carbon, possesses the interesting property of increasing in volume on passing from the solid to the liquid state.[1]

At its melting-point silver dissolves only traces of carbon, but on heating silver in the electric furnace to complete boiling, in contact with a layer of sugar carbon, it dissolves considerable carbon.

On rapidly cooling, that is, by plunging the crucible into cold water, there is formed a lump which encloses a portion of the liquid silver and the latter, on passing from the liquid to the solid state, will be submitted to a strong pressure. The carbon which is deposited in the center of the lump takes on a higher density than graphite. After the experiment the metal was dissolved in boiling nitric acid, and a powder remained which was examined with the microscope. This material was very complex. If the electrodes of the furnace or the crucibles contain silicious compounds, it contains the piles of crystals of silica, described by Marsden. Corundum and carbon silicide were also found.

This residue was submitted to the treatment previously de-

[1] When a fusion of silver which does not contain carbon is suddenly cooled in water the mass contracts on cooling; the surface of the cylinders are concave. On the contrary when silver saturated with carbon is operated on, it is observed that after the cooling, the surfaces are convex. In the latter case, the cylindrical portion was impressed with the slightest details of the crucible. It appears, therefore, that silver carbide only strongly increases in volume on passing from the liquid to the solid state. These results agree with the work of W. Chandler Roberts and T. Wrightson (*Proc. Phys. Soc.*, IV, 195), who have shown that the density of silver in the liquid state at about its melting-point is 9.51, while the density of solid silver is 10.57.

We found similar results with liquid iron and liquid aluminum when saturated with carbon.

scribed: Alternate action of boiling sulphuric acid and hydrofluoric acid and treatment with the oxidizing mixture, in the experiments which were repeated a large number of times, we always obtained only black diamonds. There frequently remained along with this carbon, transparent crystals, some of which had an octahedral appearance,[1] but slowly dissolved by repeatedly treating with concentrated sulphuric acid. They could also be removed, without attacking the black diamonds, by a fusion with potassium bisulphate at a low temperature. The residue was then treated with methylene iodide. In these experiments it is necessary to repeat many times the treatment with potassium chlorate and nitric acid in order to remove the silver which impregnates the black diamond. Under these conditions a larger yield of black diamond was obtained than in the iron fusions. The black diamonds showed either a granular appearance, or appeared as pointed plates,[2] or as masses with a conchoidal fracture, having a less bright, oily appearance, and a density which varied between 2.5 and 3.5.

This experiment, in which no transparent diamonds were made, was interesting, since it showed a series of black diamonds, whose density increased from that of graphite up to 3 or above. By treatment with bromoform we obtained a black diamond which scratched the ruby, and burned in oxygen at 1000°. This black diamond was always formed in the center of the mass; we assured ourselves of it in the following manner: If the regularly formed fusions of silver, containing no bubbles, were sawed into two equal parts, perpendicular to the base, on treating the section thus obtained with nitric acid, there was obtained, in a short time, a product of which the major portion was black diamond.

We would say that the fusion of fine silver which we used at the beginning of our experiments sometimes contained, without our knowledge, a very small quantity of gold; we found some grains of black diamond impregnated with this metal which rapidly dissolved in aqua regia.[3] This observation is significant in

[1] The crystals of carbon silicide, when broken and seen on the edge, could be taken for the octahedral points.

[2] Some specimens of carbon given by Marignac, of Geneva, to Des Cloizeaux possessed the same appearance

[3] The gold collects in the still liquid central portion. This appears to indicate that a definite alloy of gold and silver does not exist.

view of the discovery made by Des Cloizeaux of black diamonds containing small plates of gold.

E. Combustion of the Synthetic Diamonds

We have found that the crystals, obtained by means of iron and silver, cooled in water, possess the density and hardness of transparent and black diamonds; moreover, they burn in oxygen at a temperature at 700°, giving carbon dioxide. in order to definitely settle that this substance was diamond, there only remained to make a combustion by weight. This part of our investigations was the most delicate. The yield in the experiments was very small and the separation of microscopic crystals of diamond long and difficult. This small yield was due to many causes. When the fusion is suddenly cooled, the carbon in solution is not set free. Since the cooling must be rapid in order to form a solid and resisting crust on the surface of the metallic fusion, it is clear why, for ingots of 200 grams, the contents of diamonds is so small. The central portion which can yet be liquid, has not the time to deposit a large quantity of carbon before its solidification. Theoretically, a sufficient pressure must be made on the mass, saturated with carbon at a high temperature, which cools slowly. Moreover, at the moment the fusion passes from a liquid to a solid state, gas is evolved which prevents the pressure from being uniform. Finally, after the numerous treatments the liquids were decanted, and when the little diamonds were well cleaned, many of the fragments swam on the water, and we thus lost good specimens frequently.

By working with thirty fusions of silver we were able, by the methods indicated, to separate 0.006 gram of black diamond, which sank to the bottom of methylene iodide and strongly scratched the ruby. In order to make the combustion of this substance, we arranged our apparatus in the following manner (Fig. 41): A tube of Berlin porcelain, glazed inside and outside, having a length of 0.60 meter was placed in a good combustion furnace, whose temperature, measured by the electric pyrometer, was 1050°. Each end of this porcelain tube was closed by a glass stopper, cemented with Golaz cement. One of these stoppers was connected by a lead tube with a copper gasometer that was

filled with oxygen prepared from potassium chlorate and manganese dioxide, free from traces of carbon dioxide.

The oxygen passed first through two wash-bottles of baryta water which remained perfectly clear. It was then dried by means of long tubes containing pieces of potash which had been fused in a silver crucible. The other glass stopper was connected to a small tube of sulphuric acid and pumice stone, a bulb or coiled tube containing a solution of potash, and finally a small U-tube filled with pieces of fused potash. At the end of the apparatus,

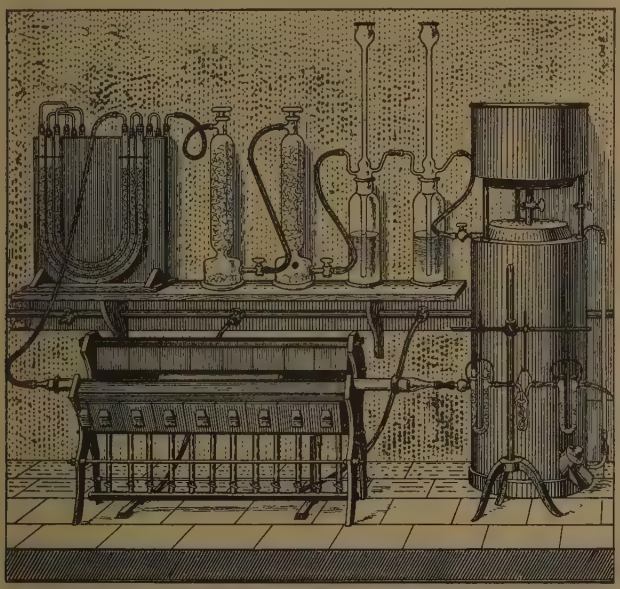

Fig. 41. Combustion apparatus.

in order to prevent the entrance of moisture, a tube of pumice stone and sulphuric acid was placed.

We began first by making blank experiments in order to obtain the limit of error of the apparatus. A platinum boat was weighed to the tenth of a milligram, then by means of a long, platinum wire was introduced into the center of the porcelain tube. The platinum wire was long enough that 0.01 meter remained outside, and could be easily grasped with pincers. The glass stopper was then

cemented on to the porcelain tube. The tubes were weighed to the tenth of a milligram and a slow current of oxygen was allowed to pass. The furnace was heated for two hours. When the experiment was over, the bulb-tube and the two U-tubes were weighed and should correspond to the original figure. The error of a blank experiment can vary from 0.001 gram to 0.0015 gram. We never found more in the six comparative experiments which were made at different times.

Combustion of the Black Diamond of Synthesis.—To make the combustion, we prepared 6 milligrams of black diamonds by means of silver fusions quickly cooled in water; the carbon was placed in the platinum boat and heated for two hours in a current of oxygen.

Weight of the boat after combustion	3.3035
" " " " before "	3.3095
" " " " in vacuum	3.3095

After the experiment:

Weight of the sulphuric acid tube	6.2675
" " " bulb tube }	1.0863
" " " solid potash }	

Before the experiment:

Weight of the sulphuric acid tube	6.2670
" " " bulb-tube }	1.0663
" " " solid potash }	

Accordingly:

Substance burned	0.006
Carbon dioxide collected	0.023

The 0.006 gram of black diamond which we burned left only a trace of ash, the weight of which was too small to determine. It gave 0.023 gram carbon dioxide; theoretically, 0.022 gram was required. This substance agrees then with the fundamental properties of carbon, giving for 1 gram 3.666 of carbon dioxide.

Combustion of Transparent Diamonds.—We then prepared transparent diamonds by means of fusions of iron quickly cooled in water and in iron filings. It was necessary to make eighty fusions to obtain, after the many treatments of which have been spoken at the beginning of this work, the small quantity of 0.0155 gram of fragments heavier than the methylene iodide. About a

tenth was black diamond, which we were unable to separate on account of their smallness. The rest consisted of transparent diamonds containing a somewhat large number of diamonds with spots obtained by the rapid cooling in the iron filings. As we have previously remarked, all of the diamonds sank in methylene iodide, scratched the ruby with great energy, and some were well crystallized. The combustion was made with all the care which a substance collected with so many difficulties merited, and the weight of the boat and tubes were first taken after a blank experiment.

Weight of the boat after the combustion	3.2928
" " " " before the "	3.3058
" " " " in vacuum	3.3083

After the experiment:

Weight of the sulphuric acid tube	6.2402
" " " bulb-tube " " " solid potash	2.8307

Before the experiment:

Weight of the sulphuric acid tube	6.2398
" " " bulb-tube " " " solid potash	2.7811

Accordingly:

Substance burned	0.0130
Carbon dioxide collected	0.0496

The weight of the substance which burned in oxygen was consequently 0.013 and the weight of the carbon dioxide collected 0.0496. Taking 12 for the atomic weight of carbon and 16 for the atomic weight of oxygen, we should theoretically obtain 0.0476 carbon dioxide.

The residue of 0.0025 which remained in the boat was particularly interesting to study. Under the microscope there were seen round, bright grains which resisted the action of oxygen at 1000°. These small, bright grains were collected and again treated with boiling sulphuric acid, then fused with potassium acid fluoride. After repeated attacks they completely disappeared. Another portion of the same material, fused with potassium bisulphate, was attacked with ease. This transparent, non-crystalline substance, which had a density above 3.5 and which scratched the

ruby, was consequently not carbon. Could it have been a variety of silicon or a silicious compound, arising from an iron rich in silicon, which was used in some of the experiments? The small quantity of material which I had at my disposal would not permit this question to be settled, but we always found the same particles when we used the electrodes rich in silica or silicious iron.[1]

After treatment of the residue from the combustion by fusion with potassium acid fluoride, there remained two or three particles of carbon silicide which were easily recognized by their appearance and crystalline form. Beside this residue, after the combustion we observed, with the microscope, traces of light ash, white or slightly ferruginous which had the appearance of the ash of the diamond. By gently blowing it disappeared, and the weight of the boat was not changed. In the particles which did not burn we found nc transparent fragments with black spots; all had burned.

By this experiment we show that 0.013 gram of combustible material gave a quantity of carbon dioxide gas which corresponds to the atomic weight of carbon. As the diamonds left a small quantity of particles which did not burn, we repeated the experiment.

New diamonds were prepared partly by means of the cylinders filled with sugar carbon and partly by means of the metallic blocks of iron and copper.[2] They sank in methylene iodide, readily scratched the ruby and did not contain black diamonds.

Combustion gave the following results:

Weight of the boat after combustion	2.1268
" " " " before "	2.1325
" " " " in vacuum	2.1325

Before the experiment:

Weight of the sulphuric acid tube	4.8670
" " " bulb-tube } " " " solid potash }	3.8310

[1] In some experiments expressly made on this point with melted iron in presence of alumina, we found some transparent powder which would not burn, amorphous, always with a corroded surface, and which under the microscope gave a reaction for alumina with caesium alum. These particles always disappeared under repeated treatment, while the diamond remained intact.

[2] These two proceedings gave the purest diamonds.

After the experiment:

Weight of the sulphuric acid tube	4.8665
" " " bulb-tube and solid potash	3.8105

Accordingly:

Material burned	0.0057
Carbon dioxide collected	0.0205

0.0057 gram of transparent diamonds gave experimentally 0.0205 gram carbon dioxide. Theory requires 0.0209. In this experiment the ash was not appreciable on the balance. These three combustions show, then, that the black and transparent fragments, having a density of 3.5 obtained in our experiments, are forms of pure carbon.

Conclusions.—In general, under the different conditions in which we worked, we have been able to obtain a variety of dense carbon, black or transparent. Some specimens presented a very good crystalline appearance; they possessed a density of 3.5, scratched the ruby, resisted twelve treatments of an oxidizing mixture of dry potassium chlorate and fuming nitric acid, the action of hydrofluoric acid and boiling sulphuric acid; finally they burned in oxygen at a temperature of about 900°, and for 1 gram of substance gave 3.666 grams of carbon dioxide. These are the properties which are possessed only by the natural diamond.

We have shown by experiment that carbon can be compared with arsenic which, in vacuum, as under the ordinary pressure, passes from the solid to the gaseous condition without taking on the liquid form. When gaseous carbon solidifies, it always appears as graphite at the ordinary pressure.

All of the varieties of amorphous carbon under the action of a sufficient increase of temperature are polymerized and attain a stable crystalline condition, in which the properties become fixed. This is graphite. At the same temperature, without passing into the liquid state, the diamond goes over into the form of graphite.

According to our views, carbon can be brought into a liquid condition, but this phenomenon is only produced under the action of a very strong pressure. In the case of great pressure, as our preceding experiments have shown, the density of carbon increases and diamond is obtained. I have been able to prepare, in the fusions of iron, cooled in lead, small diamonds having the

shape of an elongated drop, such as are sometimes found in nature. It is known that at the Cape, as in Brazil, there are found diamonds which do not possess a trace of apparent crystallization, and which have the rounded form such as those which can be obtained from a liquid held in the center of a pasty mass.

We have as another example on this point, the form of the microscopic diamonds described in the blue ground of the Cape (Fig. 20, A and C).

Carbon under pressure can take on a liquid state; it becomes transparent, its density increases, and it can solidify either by crystallizing or by assuming a round and amorphous form. An impurity, a trace of a body of the isometric system, can readily introduce a regular crystallization, or a mass of distorted crystals. If the pressure is slightly less, the diamonds are contaminated with particles of carbon which retain their black color; thus the diamonds with spots are prepared. Finally, if this pressure is still less, black diamonds, poorly crystallized, are obtained, and whose density can be less than that of the diamond.

All of these different varieties of diamond, regular octahedrons, cubes, fragments of distorted crystallization, crystals which break in time, drops, diamonds with spots, and black diamonds, have been reproduced in our work, and they justify the theoretical views that we give on the liquefication of carbon.

CHAPTER III

Preparation of Some Simple Substances in the Electric Furnace

General Remarks

The high temperature of the electric furnace enables us to extend certain reactions which have been hitherto regarded as limited, since the scale of temperature which we had at our disposal was insufficient. We know, for example, the laws of complete or incomplete decomposition of calcium carbonate by heat, laws which have been fixed in a masterly manner by Henri Debray. If barium carbonate has been regarded as a body which is not decomposed by heat alone, it appears that the temperature of the furnaces was too low to effect the dissociation.

Barium carbonate, heated in the electric furnace, is decomposed the same as calcium carbonate; it loses its carbon dioxide and leaves as residue, caustic baryta. It is also known that certain oxides could not be reduced by carbon. We mention, for example, silica, the oxides of the alkaline earths, the oxides of uranium, vanadium and zirconium. We will show that these compounds can be reduced in the electric furnace, and give the metals or the carbides which are frequently crystalline.

Metallurgy has used, in later years, currents of a larger volume for electrolysis. The recent preparation of aluminum is an example. But we think that the heat furnished by the electric arc can be also utilized, since it reduces by carbon, oxides which have heretofore been regarded as not capable of reduction. It is in this way that the use of the electric furnace permits the rapid preparation, in a fused state, of the refractory metals which have been previously obtained with much labor. The most of these elements have been heretofore studied in the form of a dark-colored powder, with somewhat variable composition and whose physical condition offered no guarantee for purity.

In order to obtain these refractory bodies by fusion, some magnesia, which is stable at the highest temperature of the arc,[1] is placed in the cavity of a furnace of lime or limestone, and on

[1] In all of our experiments, solid, liquid, or gaseous magnesia in contact with carbon remained as oxide.

it a carbon crucible is brought containing the mixture of carbon and the oxide to be reduced.

When the metal is volatile, the operation is conducted in the furnace for tubes, in a current of hydrogen, and the metallic vapors are condensed on a cold receiver. Thus calcium, strontium and barium were prepared. These metals were obtained in the form of fine powder which was impossible to unite into an ingot by fusion.[1] If the metal is not sensibly volatile it remains on the bottom of the crucible in a liquid condition and solidifies as soon as the arc is broken. This is the case with chromium, molybdenum, tungsten, titanium, uranium and other elements. Some of these preparations require a special arrangement of which we shall speak later. Most frequently, the substances obtained by this method contain variable quantities of carbon, and it is necessary, in a second operation, to refine them by means of liquid lime or an oxide of the element.[2]

We point out for each metal the precautions to take and the analysis of the various specimens.

A. Chromium

Chromium, whose discovery is due to Vauquelin,[3] has numerous applications. Its oxides and other combinations have entered into practical industry. If chromium has so far been little used as metal, it is due to the difficulty of its preparation. It had never been obtained in large quantities, and when it has been desired to utilize its valuable properties for the manufacture of chrome steel, it was necessary to prepare in the blast-furnace an alloy of iron and chromium called ferrochromium.

The presence of iron and carbon in the latter compound retarded the extension of this study, and the alloys which chromium can form with other metals were not known.

The investigations that we give here probably permit the filling in of this omission.

Preparation of Crude Chromium.—We showed in 1893 that it is possible, by means of the high temperature produced in the

[1] Finely divided mercury presents an analogous phenomenon.

[2] A large number of metals have never been obtained perfectly pure. Some contain carbon, silicon, or the alkaline metals, and it is known to-day that a very small quantity of these impurities can make a variation in the physical and the chemical properties of the elements. It, therefore, seemed important to carefully determine the state of purity of the metals obtained by means of the electric furnace.

[3] Vauquelin: "Sur une nouvelle substance métallique contenue dans le plomb rouge de Sibérie." *Ann. chim. phys.*, **25**, 21, 1797.

electric furnace, to reduce chromium sesquioxide with carbon, either in an intermittent apparatus[1] or in a continuous apparatus.[2] In the latter case we used an electric furnace which contained a carbon tube slightly inclined, taking at the upper end a mixture of the sesquioxide and carbon and allowing the liquid metal to flow from the lower end. This carbon tube was heated in our reverberatory model of electric furnace with movable electrodes, which we previously described. It was with this apparatus that we have prepared the 20 kg. of metallic chromium which served for our work.

In our first experiments, depending on whether the oxide or carbon was in excess, a carbide more or less rich in carbon was obtained. The different specimens prepared under these conditions gave the following figures:

	1.	2.	3.	4.
Chromium.....	87.37	86.25	90.30	91.70
Carbon	11.92	12.85	9.47	8.60

The crude metal thus obtained contained somewhat large quantities of carbon. We studied the different conditions of formation of this metal and were able to prepare two definite and crystalline compounds of chromium and carbon.

Carbide of the Formula Cr_3C_2.—When metallic chromium is heated in presence of a large excess of carbon for ten or fifteen minutes in the crucible of an electric furnace with a current of 350 amperes at 70 volts, there is obtained a friable lump containing crystals of chromium carbide corresponding to the formula Cr_3C_2. This carbide appears in bright scales, having a gray appearance, not attacked by concentrated hydrochloric acid, concentrated or fuming nitric acid, or aqua regia, but is slowly attacked by dilute hydrofluoric acid. Fused potash has only a slight action, while fused potassium nitrate readily attacks it. Its density is 6.47. It does not decompose water at the ordinary temperature or at 100°. It is the carbide which is stable at a high temperature. On analysis, this carbide gave the following results:

	1.	2.	Theoretical.
Chromium	86.50	86.72	86.66
Carbon.....	13.10	13.21	13.33

[1] Henri Moissan: "Préparation rapide du chrome et du manganèse à haute température," *Compt. rend.*, **116**, 349, February 20, 1893.

[2] Henri Moissan: "Sur un nouveau modèle de four électrique à réverbère et à électrodes mobiles," *Compt. rend.*, **117**, 679.

Carbide of the Formula Cr_4C.—In the numerous preparations of fused chromium that we made, we sometimes observed that the surface of the metallic ingots was covered with needles of a golden color, often having a length of 1 cm. to 2 cm. These crystals correspond to the formula Cr_4C. They were also found as bright needles in the geodes which formed inside fused chromium. Their density is 6.75.

The compound contained the following proportions of carbon and chromium:

	1.	2.	3.	4.
Chromium.....	94.22	94.02	....	94.55
Carbon.....	5.40	6.11	5.24	5.45

Crystalline Chromium.—We endeavored to refine the chromium by heating it in presence of an excess of the oxide. The metallic carbide, broken into large pieces, was brought into a carbon crucible carefully lined with chromium oxide, and covered with the same oxide. This mixture was again submitted to the heat of the electric arc, the covering of oxide melted, then the metal fused and, little by little, lost all the carbon which it contained. Chromium, thus prepared, heated in a current of chlorine, is transformed into volatile chloride without leaving a trace of carbon. The complete removal of the carbon is accomplished, but the metal is saturated with oxygen, and from the metallurgical point of view is called a burnt metal. The refining of the chromium fusion was then made in presence of fused lime, and we were able, by working on from 500 grams to 1 kilo of metal, to remove the large part of the carbon contained in the chromium. It is known that carbon and lime combine to give calcium carbide.[1]

It is this reaction that we used and it generally gave a fine-grained metal whose content of carbon varied between 1.5 and 1.9. When chromium is thus purified, although it still contains a small quantity of carbon, it crystallizes readily. We often obtained very pretty hoppers of crystalline chromium in which the crystals were 3 mm. to 4 mm. long. At first sight, these crystals have the appearance of cubes and octahedrons. Their grouping is similar to the crystalline masses of bismuth. Fremy has shown that it was possible to obtain crystalline chromium by the action of sodium on chromium chloride.

[1] Henri Moissan: "Préparation an four electrique d'un carbure de calcium cristallisé; propriétés de ce nouveau corps," *Compt. rend.*, 118, 501.

Chromium Free from Carbon.—The method of refining by fused lime, which we have described, does not give metal completely free from carbon. We observed, if the chromium was sufficiently pure, that in presence of the liquid lime and the gas of the furnace an inverse reaction was produced. All the metal was brought into the state of a double oxide of calcium and chromium which was well crystallized.

We took this double oxide which is formed readily in the electric furnace and made a lining in a furnace of quicklime and in it re-fused the chromium. Under these conditions refining takes place and a bright metal is obtained which can be easily filed and polished. This is pure chromium which, on analysis, showed no trace of carbon.

Physical Properties.—The density of pure chromium was found to be 6.92 at 20° (mean of three experiments). It differs a little, as is seen, from that heretofore given. In the oxyhydrogen blowpipe, at the point of the blue portion of the flame, crude chromium throws off bright sparks, partly burns, but only fuses superficially, due to the heat evolved in the combustion. The fusion is never complete, it is only on the surface and the fused portion is still rich in carbon. In the closed lime-furnace, which Deville and Debray used to fuse platinum, we were unable to liquefy chromium containing 2 per cent. carbon with the oxyhydrogen blowpipe in forty-five minutes. The piece of metal which was touched by the extremity of the blue flame was only partially fused on account of the phenomenon of oxidation of which we have spoken.

When chromium is quite free from carbon it burns rapidly and its combustion is more brilliant than that of iron. It oxidizes rapidly and after the experiment there remains a rounded piece of fused chromium sesquioxide.

Pure chromium is more infusible than the crude metal; its melting-point is considerably above that of platinum and cannot be reached with the oxygen blowpipe. On the contrary, in the electric furnace, fused chromium presents the appearance of a bright liquid, very fluid, possessing, in the crucible, the appearance and mobility of mercury. It is possible to remove it from the electric furnace and cast it into an ingot. By using the heat given by a current of 1000 amperes at 70 volts, we have been able, in a furnace of sufficient size, to prepare at one time 10 kilos of refined

fused chromium and cast it with ease. This fusion had the following composition:

Chromium	97.14
Carbon	1.69
Iron	0.60
Silicon	0.39
Calcium	traces

Pure chromium, free from iron, has no action on a magnetic needle.

Chromium carbide corresponding to the formula Cr_3C_2 easily scratches quartz and topaz, but is without action on corundum. The carbide Cr_4C scratches glass deeply and quartz very difficultly. When chromium is pure it has no action on quartz and scratches glass with much difficulty. Some specimens of quite pure chromium did not scratch glass.

Crude, fine-grained chromium, whose carbon content is between 1.5 and 3 per cent., can only be worked and polished with the diamond wheel. On the contrary, refined chromium, free from carbon, can be readily filed, takes the polish of iron, shows a bright luster, a little less white than the latter metal.

Chemical Properties.—Crude chromium is unchanged under the action of the carbon dioxide and moisture of the air. Pure, polished chromium is slowly tarnished after some days' exposure in moist air, but this slight oxidation is only superficial and does not continue. Chromium can be regarded as permanent in the air. Heated to 2000° in oxygen, it burns, scintillating more brilliantly than iron. Chromium filings heated to 700° in sulphur vapor evolve light and are transformed into chromium sulphide. Pure chromium, placed in a covering of carbon and heated in a strong forge fire, gives, without fusing, the carbide which crystallizes in needles and has the formula Cr_4C. Chromium, therefore, like iron, can be cemented. At the temperature of the electric furnace, it gives the crystalline compound Cr_3C_2.

Silicon combines readily with chromium. By heating a mixture of chromium and silicon in the electric furnace, a crystallized silicide is formed which has great hardness, easily scratching the ruby, not attacked by acids, aqua regia, by fused potash, or by fused potassium nitrate.

Boron combines with chromium in the electric furnace, under

the same conditions, and forms a crystalline boride, which is difficultly attacked by acids, and has great hardness.

Hydrochloric acid gas reacts on chromium at low redness, giving the crystalline protochloride. Aqueous hydrochloric acid slowly attacks chromium in the cold; more readily when heated. Dilute acid has no action at the ordinary temperature, but on boiling the action is somewhat energetic. It dissolves in dilute acid under the action of the electric current when the chromium is made the positive pole.

Boiling concentrated sulphuric acid with chromium evolves sulphur dioxide gas and the liquid assumes a dark color. Dilute acid attacks it slowly when heated, and when the reaction takes place without air excess, there is formed blue, crystalline protosulphate of chromium which we have previously described.[1]

Fuming nitric acid and aqua regia either cold or warm are without action on chromium. Dilute nitric acid attacks it very slowly.

A solution of mercury bichloride very slowly attacks powdered chromium.

Chromium, heated to 1200° in a current of hydrogen sulphide, is completely transformed into fused sulphide having a crystalline appearance. At the same temperature, carbon dioxide superficially attacks chromium and the metal is covered with a green layer of oxide mixed with carbon.

Carbon monoxide is reduced to about 1200° by this metal with the formation, on its surface, of a deposit of sesquioxide and carbonization of the chromium. This action explains the difficulty of refining; it explains why, in working with quicklime crucibles, it is impossible to obtain chromium free from carbon in the forge.

Fused potassium nitrate energetically attacks chromium at dull redness. The experiment becomes more beautiful when fused potassium chlorate is substituted for the nitrate; the chromium swims on the surface of the liquid like potassium on water, and burns brightly. Fused potash does not perceptibly attack chromium at dull redness.

Refining a Commercial Ferrochromium in the Electric Furnace.—The use of fused lime for refining a fusion rich in carbon, can have industrial application. If we begin, for example,

[1] Henri Moissan: "Sur la préparation et les propriétés du protochlorure et du sulfate de protoxyde de chrome," *Compt. rend.*, **92**, 792.

with a commercial ferrochromium containing 60 per cent. chromium, prepared in a cupola furnace, it is easy, by melting in the electric furnace under a bath of liquid lime, to deprive it of its carbon.

The following analyses demonstrate this very clearly. A ferrochromium of Saint-Chamond gave by combustion in oxygen 7.3 per cent. total carbon. After a first fusion under a layer of fused lime it contained only 5 per cent. After a second fusion it contained only 0.1 per cent. of carbon; it is, therefore, possible for a technical product, to introduce a large quantity of chromium into steel without raising the percentage of carbon.

A second series of experiments was made on a similar crystalline product which, according to our analyses, contained:

Chromium	61.81
Iron	30.02
Total carbon	7.53
Slag	0.33
	99.69

This ferrochromium was broken into pieces and fused under a bath of liquid lime. We obtained a metallic lump which had a good appearance, was fine-grained, and contained as total carbon only 4.2 per cent. The same operation was repeated, care being taken not to refine too long; the metal thus obtained gave the following results:

Chromium	64.00
Iron	35.12
Total carbon	0.70
Slag	0.22
	100.04

In this particular case, fused lime, which, in presence of carbon, forms calcium carbide, can serve to refine a crude metal by removing the carbon. These experiments will probably have some applications industrially.

Treatment of Natural Chromite in the Electric Furnace.—The ready reduction of chromium oxide in the electric furnace enables us to treat certain minerals rich in chromium, such as chrome iron which is sometimes found in nature in crystalline masses corresponding to the formula FeO, Cr_2O_3.

The mineral is reduced to a coarse powder mixed with a quan-

tity of carbon corresponding to the content of oxygen and heated in an electric furnace. By working on a quantity of 2 kilos with a current of 1000 amperes at 60 volts, we obtained in a few minutes a perfectly fused lump of ferrochromium which contained:

Chromium	60.9
Iron	31.6
Total carbon	6.1
Silicon	1.1
	99.7

This preparation, without doubt, as we said in February, 1893, will find application in the preparation of alkaline chromates. It is only necessary to add the coarsely powdered alloy to a bath of fused potassium nitrate or sodium nitrate, iron oxide becomes insoluble in water, while the alkaline chromate is soluble and can be separated and purified by crystallization.

Conclusions.—By means of the intense heat produced by the electric arc it is possible to prepare fused chromium in large quantities. This fusion which corresponds nearly to the formula Cr_4C can be refined either by fused lime or by the double oxide of calcium and chromium. The metal obtained is more infusible than platinum, it can be filed, takes a good polish, and is not attacked by atmospheric agents. It is attacked by acids with difficulty; it resists aqua regia and fused alkalies. This preparation of chromium permits the investigation of the alloys of this metal. An alloy of copper with this metal gives interesting results.

Pure copper, alloyed with 0.5 per cent. chromium, takes on a resistance almost double, and this alloy, susceptible of a good polish, alters less than copper, in contact with moist air.

B. Manganese

The use of the electric furnace has transformed the long and difficult reduction of manganese oxide into a continuous process.[1] Pure manganese protoxide is mixed with carbon and heated in the arc. When a current of 300 amperes at 60 volts is used, the re-

[1] Nickel and cobalt oxides are also rapidly reduced by carbon in the electric furnace. We obtained fusions which contained:

	1.	2.	3.
Nickel	86.10	87.62	94.40
Total carbon	13 47	11.90	6.19

A specimen of cobalt prepared with an excess of the oxide gave in three successive analyses:

Per cent. of carbon	0.726	0.732	0.741

duction is complete in five or six minutes. There remains on the bottom of the crucible a lump of 100 grams to 120 grams of manganese carbide. The reduction can be made more slowly by using an arc of 100 amperes at 50 volts. In this case it takes ten to fifteen minutes.

When an excess of carbon is used, the manganese is saturated with carbon and the fusions, on analysis, gave the following results:

	1.	2.	3.	4.
Manganese	85.00	85.82	90.60	94.06
Carbon	14.59	13.98	10.20	6.35

If the reduction is made in presence of an excess of oxide, the quantity of carbon is greatly diminished, and in some fusions only 4 to 5 per cent. of carbon was obtained. When the fusion of manganese thus prepared contains only a little carbon it can be preserved in open vessels, but when the quantity of carbon is increased the moisture of the air decomposes it. Small pieces placed in water oxidized in twenty hours with the formation of hydrogen and hydrocarbons. This decomposition by the moisture of the air is more energetic as the content of carbon approaches manganese carbide, Mn_3C, discovered by Troost and Hautefeuille. We will return later to the properties of manganese carbide.

When a large quantity of metallic manganese is prepared by a more powerful arc, the ready volatilization of manganese renders the yield very small, a considerable quantity of the metal being lost by volatilization. To avoid the action of too strong heat, we heated the mixture to be reduced in a carbon crucible provided with a cover. Under these conditions, we obtained metallic masses of 400 grams to 500 grams having the following composition:

	1.	2.
Manganese	95.20	96.12
Carbon	4.50	3.60

This crude manganese when heated in the forge in a layer of oxide can be superficially refined and gives a soft metal which can be easily filed. When manganese contains no carbon, it does not scratch glass. By starting with native manganese dioxide as pure as possible (97.5 per cent.), previously roasted in a Perrot furnace, we obtained with a current of 500 amperes at 50 volts in a closed crucible a fusion which gave on analysis:

	1.	2.
Manganese	89.78	91.13
Total carbon	7.59	6.41
Slag	2.06	1.78

The yield was 96 per cent. of the oxide used in the experiment. I believe that this reaction is applicable to the technical preparation of metallic manganese, and as the refining of this fused metal is effected by the presence of an excess of oxide, it is possible to obtain manganese free from carbon and silicon.

C. Molybdenum

Molybdenum is obtained in the form of powder by reduction of the dioxide at low redness in pure hydrogen, then heating the metal obtained in a current of hydrochloric acid gas. Heretofore molybdenum has been regarded as infusible. Henri Debray[1] has, with difficulty by the oxyhydrogen blowpipe, fused an impure molybdenum containing 4 to 5 per cent. of carbon.

Preparation of Molybdenum.—To prepare molybdenum, we started with pure ammonium molybdate which was powdered and introduced into a crucible of refractory clay, holding 1 kilogram. The covered crucible was heated an hour and a half in a Perrot furnace. After cooling, the oxide appeared as a dense powder, violet-gray in color, corresponding to the formula MoO_2.[2] One operation gave 760 grams to 770 grams of oxide. This oxide, mixed with carbon, was heated in the crucible of the electric furnace. In the preliminary experiments, made with an excess of carbon, we obtained, on heating seven or eight minutes with a current of 350 amperes at 70 volts, fusions which contained:

	1.	2.	3.
Carbon	9.77	9.88	9.90

We then undertook the preparation under the following conditions: Molybdenum oxide, roasted as we have described, was mixed with finely powdered sugar carbon in the proportion:

	Grams.
Oxide	300
Carbon	30

In this mixture, the dioxide was in considerable excess of the carbon. The powder was carefully introduced into a carbon crucible and submitted to the action of an arc produced by a cur-

[1] Debray: "Recherches sur le molybdène," *Compt. rend.*, **46**, 1098 (1898).

[2] Method of Bucholz for the Preparation of the Dioxide.

rent of 800 amperes at 60 volts for six minutes. The metal should not be so completely fused that a solid layer of the mixture remains in contact to the crucible which would be strongly attacked by the liquid molybdenum. Under these conditions, a metal completely free from carbon is obtained, and it is easy to obtain more than 2 kilograms in an hour. If the operation lasts more than six minutes, the molybdenum becomes liquid, attacks the crucible, becomes carbonized and appears as a gray mass, very hard and brittle.

In another experiment, using an electric furnace having a cavity of 5 to 6 liters capacity, we have, at one time, made 8 kilograms of molybdenum which could be readily cast. This experiment was repeated and gave an ingot of 10.3 kilos.

Since the publication of my work in the *Comptes rendus de l'Académie des Sciences*[1] one of my students, Guichard, has obtained a crude molybdenum in considerable quantity by reduction of natural molybdenite with carbon in the electric furnace;[2] the fusion thus prepared contained no sulphur. On analysis, it gave:

Molybdenum	91.80
Iron	2.10
Total carbon	6.64

This reduction appears important to me since, molybdenum containing more or less carbon can be obtained by a simple treatment of the mineral in the electric furnace.

Crude Molybdenum.—It has a density of 8.6 to 8.9, according to its carbon content. When it is saturated with carbon it is much less fusible than molybdenum. When it is rich in carbon, it is gray and brittle; with 2.5 per cent of carbon, it becomes white and can be broken, only with difficulty, on the anvil. It possesses all the characteristics of the molybdenum studied by Debray. It rapidly dissolves carbon and when cooled deposits the latter as graphite, exactly as cast iron does; yet, when saturated with carbon, it gives a carbide, crystallizing in fine needles.

The gray, crude molybdenum is very hard; it scratches steel and quartz. When fused, it gives a very mobile liquid which can be cast, throwing bright sparks in the air and evolving heavy

[1] H. Moissan: "Preparation au four électrique de quelques métaux réfractaires; tungstène, molybdéne, vanadium," *Compt. rend.*, **116**, 1225, May 29, 1893; and Préparation du molybdéne pur fondu," *Compt. rend.*, **120**, 1320, June 17, 1895.

[2] Guichard: *Compt. rend.*, **122**, 1270.

fumes of molybdic acid. These fusions, on analysis, gave the following figures:

		White cast.		Gray cast.	
	1.	2.	3.	4.	5.
Molybdenum	95.83	...	...	...	92.46
Combined carbon	3.04	3.19	2.53	4.90	5.50
Graphite	0.00	0.00	0.00	0.00	1.71
Slag	0.74	0.53	0.62	...	...

Carbide of Molybdenum.—This compound is prepared by heating molybdenum dioxide with an excess of carbon in the electric furnace. The best proportions to take are: Dioxide 250 grams, carbon 50 grams. Time of heating, eight to ten minutes, with a current of 800 amperes at 50 volts. When an excess of carbon is used, it is found in the mass as graphite. The fusion obtained has a bright white, crystalline fracture. It cleaves readily; and when it is crushed on the anvil, small, elongated, well-crystallized prisms can be separated. Its density is 8.9 and its composition corresponds to the formula Mo_2C.

Analysis.—In the different specimens studied in this chapter, the molybdenum, after treatment with nitric acid, was precipitated as mercurous molybdate, and finally weighed as dioxide. When the carbide contained no graphite, the carbon was separated by pure dry chlorine, then estimated by combustion in oxygen, weighing the carbon dioxide obtained. By this method the carbon content is always a little low. The following results were obtained:

	6.	7.	8.	Theoretical for Mo_2C.
Molybdenum	93.82	...	...	94.12
Combined carbon	5.62	5.57	5.48	5.88
Graphite	...	...	...	...
Slag	0.17	...	...	...
	99.61			

If the carbide contains graphite, it is treated with nitric acid in a flat-bottomed flask through which a current of oxygen passes. The gas evolved passes through a tube filled with hot copper oxide; the water vapor is removed by a tube containing sulphuric acid and pumice and the carbon dioxide is collected by potash. From the increase of the weight of the potash tubes, the carbon dioxide and carbon are obtained. The acid liquid in the flask, after filtration and washing, gives the graphite, and the molybdenum is

then determined by mercurous nitrate. This method gave the following results:

	9.	10.
Molybdenum	92.60	91.90
Combined carbon	5.15	5.43
Graphite	1.61	1.98

By calculating without the graphite and reporting the molybdenum and carbon, the following figures are obtained:

	9.	10.	Theoretical for Mo_2C.
Molybdenum	94.45	94.10	94.12
Combined carbon	5.55	5.90	5.88

Pure Fused Molybdenum.—Pure molybdenum has a density of 9.01. It is as malleable a metal as iron. It can be filed and polished with ease, and can be worked hot. It scratches neither quartz nor glass. Free from carbon and silicon, it oxidizes in the air at a low red-heat. It can be kept for many days in ordinary water or water charged with carbon dioxide, without alteration. Below dull redness it becomes covered in the air with an iridescent film like steel. At about 600°, it commences to oxidize and gives molybdic acid which slowly volatilizes.

A piece of molybdenum heated for several hours in an inclined porcelain tube in a combustion furnace gives a deposit of crystals of molybdic acid in the upper part of the tube. The metal does not become covered with any other oxide, and finally disappears, giving a beautiful crystallization of molybdic acid. Heated in the blast-lamp it burns without fusing, giving copious fumes of molybdic acid and a blue fusible oxide. Heated in a current of pure oxygen, it takes fire between 500° and 600° and if the current of oxygen is rapid the combustion continues without the aid of outside heat.

The combustion is accompanied by light and while in progress makes a beautiful experiment. Fused potassium chlorate attacks molybdenum with violence. The chlorate is fused and on its surface a piece of molybdenum is dropped when the latter takes fire, revolving on the liquid. The temperature rapidly rises; the molybdenum burns with flame and evolves copious white fumes of molybdic acid, which remain in suspension in the air in the form of light, white filaments. Sometimes the piece of molybdenum is raised to so high a temperature that it penetrates the side of the vessel in which the metal is fused.

Fused potassium nitrate under the same conditions gives a similar reaction, though less violent, forming alkaline molybdate. A mixture of molybdenum and lead dioxide heated in a test-tube gives great evolution of light and heat.

Sulphur does not act at 440°, but hydrogen sulphide at 1200° transforms molybdenum into an amorphous blue-gray sulphide, which has the properties of molybdenite and which, rubbed on paper, leaves a black streak.

Fluorine does not attack lumps of the molybdenum in the cold, but when the metal is coarsely pulverized it forms a volatile fluoride without evolution of light. Chlorine attacks molybdenum at dull redness without apparent evolution of light. With bromine the reaction takes place at a cherry-red heat and without great intensity.

Iodine is without action at the softening-point of glass.

The fluorides of silver, zinc and lead are decomposed, but without formation of volatile fluorides. Slightly heated phosphorus pentachloride attacks molybdenum, giving a volatile chloride which readily alters in presence of the moisture of the air, becoming blue. This reaction takes place with most of the compounds of molybdenum: Metal, oxides, sulphide, molybdic acid and molybdates; it can be used as a rapid detection of metallic molybdenum and its compounds. It is made in the following manner: In a test-tube there is placed a piece of the substance to be tested, a little phosphorus pentachloride is added and slowly warmed. Reddish vapors of chloride and oxychloride of molybdenum appear and condense in more or less dark brown rings. When the quantity of molybdenum is very small, the rings are scarcely visible. It is only necessary to allow it to stand a few minutes in a moist place when an intense blue color, due to the formation of a hydrated chloride, appears.

The action of the halogen acids on pure molybdenum is much the same as on cast molybdenum. Their action has been described by various observers: Bucholz, Berzelius, Debray. We would mention that while hydrofluoric acid does not attack molybdenum it is only necessary to add a drop of nitric acid in order to start the action, when it proceeds energetically. In presence of a mixture of equal parts of the two acids, solution is complete; a rose-colored liquid is formed which, with ferrocyanide, gives

an intense red-brown coloration, but no precipitate. After several hours the mass becomes gelatinous.

In a current of nitrogen at 1200° molybdenum, in lumps or in powder, does not form nitride.

Phosphorus heated to the fusing-point of glass has no action on it.

Boron unites with molybdenum at the temperature of the electric furnace, giving a fused mass of an iron-gray color, containing geodes lined with prismatic needles. Under the same conditions, silicon gives a crystalline silicide, infusible in the oxyhydrogen blowpipe. The action of carbon is worthy of note. We have described the action of carbon on liquid molybdenum and will not review it.

Pure molybdenum, such as we have described, is somewhat soft, is easily filed and does not scratch glass. If a piece of molybdenum is heated for some hours, to about 1500° in a mass of powdered carbon, it is cemented, takes up a small quantity of carbon and its hardness increases. Pure molybdenum, heated in a current of oxygen, does not render baryta water turbid. When the metal has been cemented, it gives a white precipitate of barium carbonate when heated to redness in a current of oxygen. It can then scratch glass. By heating to about 300°, and quickly plunging into cold water, it is tempered, and becomes so hard that it scratches quartz crystals. On the other hand, a piece of crude molybdenum containing 4 per cent. of carbon, and possessing great hardness and brittleness, when heated for several hours in a layer of molybdenum dioxide was refined and its surface could be filed and polished. I attribute this decarbonization of the solid cast metal at a temperature far below its melting-point to the easy diffusion of the vapors of molybdic acid through the metal. I think that these properties can find some application in metallurgy.

When a metal is saturated with oxygen, as that obtained in the first period in the Bessemer process, the oxygen can be removed by adding manganese, which is more easily oxidized than iron, and passes into the slag (Troost and Hautefeuille). It has been proposed to use aluminum, which gives good results, since it combines readily with the oxygen; but this metal is not convenient as it gives solid alumina. I think that molybdenum could be used under the same conditions; it would have the advantage:

1. Of forming a volatile oxide, molybdic acid, which is immediately evolved in gaseous condition, stirring up the entire mass.

2. By using a slight excess, it would leave in the bath a metal as malleable as the iron and which, like it, can be tempered.

Powdered molybdenum, which has been tried, does not give the same results, as it rapidly burns on the bath in contact to the air, without performing any useful action.

ANALYSIS OF PURE MOLYBDENUM.

	11.	12.	13.	14.
Molybdenum	99.98	99.37	99.89	99.78
Carbon	0.00	0.01	0.00	0.00
Slag	0.13	0.28	0.08	0.17

CONCLUSIONS.—Pure and fused molybdenum can be obtained in the electric furnace. The metal in pure condition has a density of 9.01. It is as malleable as iron; in the cold it can be filed, and when heated can be worked. Heated in a layer of carbon, it is cemented and on tempering forms a steel of much greater hardness than pure molybdenum. Inversely, crude molybdenum heated in a mass of oxide loses its carbon, is refined and takes on the properties of pure molybdenum.

In presence of an excess of carbon, molybdenum in the electric furnace gives a definite carbide which is crystalline and stable, having the formula Mo_2C.

D. Tungsten

On the 29th of May, 1893,[1] I showed that crude tungsten could be prepared in large quantities in the electric furnace, and that it could be subsequently refined by fusing the metal in presence of an excess of tungstic acid.

Preparation of Crude Tungsten.—The mixture of tungstic acid and carbon is placed in a crucible in the electric furnace and in about ten minutes, with a current of 350 amperes at 70 volts, there is obtained a metallic fusion of about 120 grams. The hard, bright metal, thus prepared, has a white color, and a fine grain when no excess of carbon is present. On the contrary, samples 3 and 4 had a micaceous appearance and contained plates of graphite. Four samples gave:

	1.	2.	3.	4.
Total carbon	0.64	2.74	4.56	6.33

[1] H. Moissan : "Préparation, au four électrique, de quelques métaux réfractaires : tungstène, molybdène, vanadium," *Compt. rend.*, **106**, 1225, May 29, 1893.

Preparation of Pure Metal.—Tungsten can be obtained in pure condition by directly heating in the electric furnace a mixture of tungstic acid and sugar carbon. The proportions used are the following: Pure tungsten acid, 800 grams; pulverized sugar carbon, 80 grams. This mixture contains an excess of tungstic acid. Tungsten, being a difficulty fusible metal, should be heated for ten minutes, with a current of 900 amperes at 50 volts. A mass is obtained which appears fused on the surface, but inside is porous, and only touches the carbon crucible in places. By avoiding the complete fusion of the metal, the carbon of the crucible does not interfere, and the excess of tungstic acid is volatilized.

Physical Properties.—Tungsten, prepared in the electric furnace as we have described, can be obtained entirely free from carbon. Deslandres, who was kind enough to examine it with the spectroscope, found that the metal was very pure.[1] When it is porous, like iron, it has the property of being welded by hammering much below its melting-point. It can be easily filed, and when free from carbon, does not scratch glass.

A piece of malleable tungsten was heated in a crucible lined with wood charcoal, at the temperature of the forge for an hour and a half. The crucible containing the metal was surrounded by a titanium-containing layer to prevent the action of nitrogen. On cooling, the outside portion of the metallic lump contained carbon, and its hardness was so much increased that it scratched the ruby. Pure tungsten is thus readily cemented and this explains the various results heretofore obtained when an attempt was made to fuse the metal. It is known that Riche has been able to fuse tungsten by carbonizing it in an arc given by 200 Bunsen cells.[2] Similarly, Siemens and Hutington[3] have fused in very small quantities, in the electric furnace, tungsten containing 1.8 per cent. of carbon. Pure tungsten is more infusible than chromium and molybdenum.

The density of pure tungsten has been found to be 18.7. The metal exerts no action on the magnetic needle.

Chemical Properties.—Fluorine attacks tungsten at the ordinary

[1] This tungsten, with the spectroscope, showed only very weak calcium lines.

[2] Richie: "Recherches sur le tungstène et ses composès," *Ann. chim. phys.*, 3e série, **50**, 5 (1857).

[3] Siemens and Hutington: "On the Electric Furnace," British Association, 1883 and *Ann. chim. phys.*, 5e série, **30**, 465 (1883).

temperature, with evolution of light giving a volatile fluoride. The action of the halogen acids has been studied in detail by Riche and Roscoe in 1872,[1] so we did not repeat the work.

Nitrogen and phosphorus do not combine with tungsten at redness. Heated in the electric furnace with silicon and boron, tungsten gives compounds having a crystalline metallic appearance and which easily scratched the ruby. At 1200°, carbon dioxide is reduced by tungsten with the formation of the blue oxide and without depositing carbon.

Fused tungsten is not perceptibly oxidized in moist air, but it is, in time, attacked by water charged with carbon dioxide. Sulphuric and hydrochloric acids attack it only with difficulty; the same is true with hydrofluoric acid, while a mixture of hydrofluoric and nitric acids rapidly dissolves it.

Oxidizing agents, such as lead dioxide and fused potassium chlorate, attack the pulverized metal with evolution of light.

Fused sodium carbonate slowly dissolves it, but a mixture of carbonate and nitrate attacks it rapidly.

Analysis.—The metal was fused with a mixture of alkaline nitrate and carbonate, and the tungsten was precipitated as mercurous tungstate.

From samples which could be easily filed and which did not scratch glass, the following analysis was obtained:

	1.	2.	3.
Tungsten	99.76	99.82	99.87
Carbon	0.00	0.00	0.00
Slag	0.18	0.09	...

Tungsten Carbide.—When the heating is prolonged, in the preparation of tungsten, the metal completely fuses, attacks the crucible, unites with the carbide, giving a crude metal. We have shown the carbon content of these fusions.

In the presence of an excess of carbon, tungsten forms a definite carbide having the formula W_2C. This carbide is iron-gray and is very hard, scratching corundum deeply. Its density at 18° is 16.06. It gives about the same reactions as the metal, but is more easily attacked than the latter. It takes fire in fluorine in the cold, burns at about 500° in oxygen, giving tungstic acid and carbon dioxide, and in the liquid condition readily dissolves carbon which, on cooling, separates as graphite. Like the metal,

[1] Roscoe: *Manchester Lit. Phil. Soc. Proc.*, **11**, 79 (1872).

the acids attack it only very slowly, but boiling nitric acid easily dissolves it.

Fused potassium chlorate, or a mixture of carbonate and nitrate oxidizes it with evolution of light. At redness it burns in nitrous and in nitric oxides.

Analysis.—The total carbon was estimated by chlorine, and the graphite, separated from the amorphous carbon by fuming nitric acid, was weighed on a tared filter. The tungsten was precipitated as mercurous tungstate.

	1.	2.	3.	Theoretical for W_2C.
Combined carbon	3.22	3.05	3.09	3.16
Tungsten	96.60	96.78	96.95	96.84

Tungsten Carbide.—By heating tungsten in the electric furnace with an excess of carbon, the carbide W_2C is obtained. Williams[1] heated the following mixture in the electric furnace:

	Grams.
Tungstic acid	120
Petroleum coke	20
Iron	150

He obtained a well-defined carbide having the formula WC, mixed with a large quantity of iron and double carbide. This body was isolated by removing most of the impurities with the magnet, separating the graphite by its density and removing the last traces of impurities by chlorine.

Analysis gave the following results:

	1.	2.	3.	Theoretical for WC.
Tungsten	93.55	93.52	93.60	93.88
Carbon	5.87	6.20	6.08	6.12

Double Carbide of Iron and Tungsten.—On heating a mixture of tungstic acid, iron and petroleum coke in the electric furnace, Williams[2] obtained a mixture of tungsten carbide and a double carbide of iron and tungsten. By means of the magnet, it is possible to separate the crystals, which are treated with aqua regia. The most of the crystals pass into solution while there remains a bright metallic powder which corresponds to the formula $2Fe_3C,3W_2C$. The slight difference observed in the analysis is due to a small quantity of a second double carbide which has not been entirely separated. Analysis gave:

[1] P. Williams: *Compt. rend.*, **126**, 1722.

[2] P. Williams: *Ibid.*, **127**, 420.

	1.	2.	3.	Theoretical for $2Fe_3C,3W_2C$.
Tungsten	72.0	71.4	71.3	73.6
Iron	23.1	23.5	23.8	22.4
Carbon	3.8	4.2	...	4.0

CONCLUSIONS.—Tungsten is readily prepared in the electric furnace by reduction of tungstic acid with carbon. If the melting-point is not reached, the metal can be obtained in a very pure condition.

By working in presence of an excess of carbon or by fusing the metal in a carbon crucible, there is obtained a definite carbide of the formula W_2C, which dissolves carbon and again deposits it as graphite.

Pure tungsten can be filed and worked; it is readily cemented, does not act on the magnetic needle and has a higher melting-point than chromium or molybdenum.

E. Uranium

Metallic uranium was obtained for the first time by Péligot[1] by reducing uranium chloride with potassium in a platinum crucible. In this preparation a gray powder is obtained in which some small, metallic globules are found.

Different investigators have slightly modified this reaction, and in 1886 Zimmermann[2] undertook the study of the properties of uranium and obtained the metal by reduction of uranium chloride with sodium. The metallic globules obtained in this preparation were few in number. Their fusion was due to the intense heat developed by the action of the alkali metal on the chloride. We repeated all of these experiments. When a platinum crucible is used, the uranium is always contaminated by this metal. In Zimmermann's preparation, the uranium contains about 2 per cent. of iron and a small quantity of sodium. Moreover, when this method is employed the entire uranium powder contains nitrogen and frequently oxygen.

We will show later that metallic uranium has a much greater affinity for nitrogen than has been known. We thought that this action of the alkaline metals could be made under better conditions by use of a double compound of sodium and uranium.

Preparation of the Double Chloride of Uranium and Sodium,

[1] Peligot: "Recherches sur l'uranium," *Ann. chim. phys.*, 3e série, **5** (1842).
[2] Zimmermann: *Ann. Chem.* (Liebig), **213**, 290, and **216**, 1.

UCl_4,2NaCl.—When the vapors of uranium chloride are allowed to act on sodium chloride at a low-red heat, a double chloride is obtained which, on cooling, assumes a crystalline appearance, has an apple-green color, melts at about 390°, is soluble in cold water and is decomposed by alcohol.

This preparation is readily carried out in a tube of Bohemian glass by preparing at one end uranium chloride by the action of chlorine or uranium carbide and conducting this chloride over pieces of sodium chloride heated to dull redness at the other end of the tube. The solid alkaline chloride becomes colored by absorption of the vapors of uranium chloride, then fuses. Uranium chloride, UCl_4, has great affinity for water, fumes in the air and is difficult to handle. On the contrary, the crystalline double chloride is much less hygroscopic and does not decompose so readily. When fused, it becomes a stable liquid which, apparently, gives off no vapors.

Reduction of the Double Chloride by the Alkaline Metals.—The reduction was made in a cylinder of thick iron closed by a screw-plug. Alternate layers were made of a mixture of 300 grams of the double chloride and 100 grams of freshly cut sodium. The apparatus was closed and placed in a good wood fire where it was heated for twenty-five minutes. The heat evolved in the reaction was sufficiently great to raise the tube to a white heat in a few minutes. On cooling, the cylinder was opened, and the pulverulent material which it contained was first treated with 96 per cent. alcohol to remove the excess of sodium, then quckly washed with cold water which had been previously boiled, and finally with alcohol and ether.

Preparation of Uranium in the Electric Furnace.—At the highest temperatures of our ordinary furnaces the various oxides of uranium are not reduced by carbon. This is not true at the high temperatures which can be reached in the electric furnace.

To obtain the metal, uranium nitrate which can be prepared very pure, is heated in a porcelain dish[1] when the green oxide is obtained which corresponds to the formula U_3O_8. This oxide is mixed with sugar carbon and strongly pressed in a carbon crucible. On submitting this mixture in the electric furnace, to the action of an arc of 450 amperes at 60 volts, reduction is effected in a short

[1] See later the "Preparation of Uranium Carbide."

time. On cooling, the crucible is found to contain a metallic lump having a bright fracture. The yield of uranium in this preparation is good. An experiment twelve minutes long gives a lump of 200 to 220 grams. By this means a crude metal is obtained whose carbon content varies with the excess of oxide or carbon in the mixture. Qualitative analysis of the first samples showed only uranium, carbon and a little nitrogen. Various determinations gave the following results:

	1.	2.	3.	4.	5.
Uranium	86.25	89.46	89.10	95.70	97.60
Carbon	13.50	11.03	10.24	5.02	2.06

In another series of experiments, we used the following mixture:

	Grams.
Uranium	500
Sugar carbon	40

About 500 grams of this mixture were placed in a carbon crucible and heated in the electric furnace for seven or eight minutes with a current of 800 amperes at 45 volts. A fused ingot of 350 grams was obtained. The metal prepared under these conditions, if the heating has been well conducted, contains little or no carbon. On the other hand, a small quantity of oxide can be found in a burned metal of which the physical properties are considerably changed. If the heating lasts too long, the metal readily carbonizes, becomes saturated, forming the crystalline carbide U_2C_3. In order to prevent the action of nitrogen, it is well to make the experiments in a carbon tube which is closed at one end, in the manner previously described.

Refining the Crude Uranium in the Forge.—When a uranium is prepared which contains 0.1 to 0.5 per cent. of carbon by the above proceeding, the outside surface of the pieces can be refined by heating it in the forge for several hours in a layer of the green oxide of uranium. To make this experiment, the crucible which contains the oxide of uranium and the metal is placed in another crucible which is filled with finely powdered titanium-containing material. The omission of this precaution gives a yellow-colored metal covered with nitride.

Preparation of Metallic Uranium by Electrolysis.—The double chloride of uranium and sodium that we described is very easily electrolyzed. At the negative pole it gives a sponge of uranium which often contains small crystals of the metal. To make the

operation regular there should be a difference of potential of 8 to 10 volts. We generally used a current of 50 amperes. The bath is kept liquid by the action of the heat of the current.

The electrolysis was made by means of electrodes of pure carbon and the chloride was placed in a cylindrical porcelain vessel. This vessel was closed by a glazed porcelain plate through which passed the two electrodes and a glass tube bent at right angle. The latter permitted the introduction of a current of a dry hydrogen free from nitrogen, on top the fused salt. After becoming perfectly cool, the contents of the crucible were treated with ice water and quickly washed with alcohol, since very finely divided uranium decomposes water at the ordinary temperature. This uranium was crystalline; some parts which were close to the electrodes appeared as good crystals, 1 mm. long.

When an iron electrode is used, it is possible to obtain, by this proceeding, silver-white alloys of uranium and iron, which can be easily filed and which have a fine grain.

Physical Properties.—When uranium is quite pure, its color is absolutely white, less blue than iron, and can take on a polish. If the metal is yellow-colored it is always possible to detect the presence of nitrogen. Pure uranium is easily filed, it does not scratch glass; can be slowly carbonized when gently heated in a layer of carbon and then can take a temper. When it is entirely free from iron, it is not magnetic; we have already drawn attention to this point. Uranium can be distilled in the electric furnace and can be collected by condensation of the vapor in small metallic spheres free from carbon, which do not act on the magnetic needle.

Chemical Properties.—Finely powdered uranium, prepared by electrolysis, takes fire in fluorine, burns brightly, and gives a green-colored volatile fluoride. Chlorine attacks it at 180°; bromine at 210°, both with evolution of light. The same reaction takes place in iodine vapor at about 260°, with formation of uranium iodide. All of these reactions are complete. The metal obtained by Zimmermann was not attached by iodine vapor and in a current of chlorine gave an incomplete reaction, leaving considerable residue in the boat.

Hydrochloric acid gas attacks uranium with evolution of light

at dull redness, giving a stable chloride, which, with water, gives a green solution. Hydriodic acid attacks it at redness.

Finely powdered uranium burns in pure oxygen at a temperature of 170°, forming dark green oxide. When fused uranium is thrown on porcelain, or when the fragments are shaken in a glass flask, it emits bright sparks by combustion of a small quantity of the metal. It shows in this case, but with greater brilliancy, a phenomenon analogous to the combustion of particles of iron which takes fire by simple friction in the air. It is possible to use this fused uranium to make tinder boxes or fuses, since it gives good sparks, is rich in carbon and is friable. I think that it would be better to substitute for the crude uranium an alloy of iron and uranium containing a small quantity of carbon.

Uranium reacts with sulphur, at about 500°, forming a black sulphide which is slowly attacked by hydrochloric acid, giving hydrogen sulphide. It combines with selenium with evolution of light. As we have already remarked, uranium unites with nitrogen with great energy. Pieces of the metal heated in a current of nitrogen to 1000° are covered with a yellow layer of nitride. Powdered uranium acts on ammonia gas at dull redness without evolution of light, giving hydrogen gas, and leaving a black, crystalline powder whose investigation we reserve. Very finely powdered, pure uranium slowly decomposes water at the ordinary temperature and more rapidly at 100°. In this property it closely resembles iron. Troost and Hautefeuille have shown that reduced iron decomposes water at its boiling-point. Fused uranium becomes covered with a layer of oxide in contact with water, and the action is increased by the presence of carbon dioxide.

Analysis.—In all of our work, the uranium was separated and weighed as the oxide U_3O_8 and the carbon as carbon dioxide.

The double chloride of uranium and sodium on analysis gave the following results:

	1.	2.	3.	Theoretical.
Uranium	47.9	47.7	48.20	48.08
Sodium	..	...	10.10	9.21
Chlorine	42.3	42.4	42.01	42.68

Metallic uranium, prepared by sodium, gave:

	1.	2.
Uranium	99.40	99.28

The specimens always contained traces of alkali metals.

The metal prepared in the electric furnace contained:

	1.	2.	3.	4.
Uranium	99.121	99.106	99.021	99.520
Carbon	0.168	0.601	1.356	0.005
Slag	0.187	0.204	0.303	0.421

Uranium, prepared by electrolysis, gave:

	1.	2.
Uranium	99.27	99.48
Insoluble in nitric acid	0.52	0.27

Conclusions.—Metallic uranium can be obtained either by decomposing the double chloride of uranium and sodium, or by the electrolysis of the same compound, or better by the reduction of uranium oxide with carbon in the electric furnace. These three methods give good yields, and we had occasion in our investigations to prepare more than 15 kilograms of metallic uranium. Uranium can be obtained crystalline; the pure metal has properties which closely resemble iron; it can be filed, carbonized, tempered and oxidized like it. It combines with oxygen more readily than does iron; in fine powder it slowly decomposes cold water; its action on the halogens is also more energetic.

It possesses a powerful affinity for nitrogen, and if, in its preparation, the greatest precautions are not taken to avoid the action of this element, it will always contain some.

The metal, when free from iron, has no action on the magnetic needle and is considerably more volatile than iron in the electric furnace.

F. Vanadium[1]

The work of Roscoe has shown how difficult the preparation of this element is. This chemist has shown that by reduction of vanadic acid with carbon only a silicide is obtained, which is scarcely fusible at the temperature of the wind furnace. Roscoe was able to surmount the numerous difficulties which this preparation presented, and by reducing vanadium dichloride with pure dry hydrogen obtained metallic vanadium. He observed, nevertheless, that the metal obtained in form of a powder still contained a small quantity of oxygen and 1.8 per cent. of hydrogen.

The preparation of crude vanadium is one that has presented the greatest difficulties in the electric furnace. We began with pure ammonium metavanadate which, on roasting, gives a yellow-

[1] *Compt. rend.*, **116**, 1225, May 29, 1893, and **122**, 1297, June 8, 1896.

brown and rather easily fusible, vanadic oxide. This oxide was mixed with sugar carbon, and when placed in an arc of several centimeters produced by a current of 350 amperes at 70 volts, was not reduced. The arc must be allowed to play in contact with the powder and the operation must be continued twenty minutes in order to obtain, and only on the surface of the mixture, small metallic granules the size of a pea. We then used an arc of much larger current. By using an arc furnished by a 150-horse-power dynamo giving 1000 amperes at 70 volts, we were able to obtain complete reduction of the oxide and the fusion of the carbide at the same time.

The content of total carbon in the fusions containing graphite, prepared under these conditions, is as follows:

	1.	2.	3.
Carbon	25.47	25.68	17.56

Thanks to Heern who placed at our disposal a considerable quantity of ash from a vanadiferous coal,[1] I have been able to continue and extend the work.

Treatment of the Vanadiferous Ash.—The ashes mixed with pieces of coal which was given to me contained 8 to 10 per cent. of vanadic acid. They were roasted in a muffle to destroy all the carbonaceous matter. The content of vanadic acid was thus raised to 38 per cent.

500 grams of the ash were placed in a 2-liter flask and treated on a sand-bath with nitric acid, to which a small quantity of hydrochloric acid was added from time to time. It was taken up with water and the insoluble residue washed. After filtration through a linen cloth, all of the filtrates were united and evaporated to dryness; the residue was taken up with 10 per cent. ammonia and gave a solution of ammonium vanadate, which was concentrated, then precipitated with nitric acid when crude vanadic

[1] M. Mourlot has given as the analysis of this ash the following figures: *Compt. rend.*, 117, 546.

Portion soluble in acids:		Portion insoluble in acids:	
Vanadic acid	38.5	Silica	13.6
Sulphuric acid	12.1	Alumina	5.5
Phosphoric acid	0.8	Ferric oxide	9.4
Ferric oxide	4.1	Magnesia	0.9
Alumina	4.0		29.4
Lime	8.44		
Potassium oxide	1.8		
	69.74		

acid was obtained. The insoluble residue was extracted a second time with 10 per cent. ammonia; it gave additional vanadate, which was similarly treated with nitric acid.

The crude acid thus obtained was purified according to the method of L'Hôte.[1] The vanadium was converted into vanadyl chloride and the latter decomposed by water. Vanadyl chloride was obtained at 250° and was purified by fractionating 150 grams from a bulb. The vanadyl chloride distilled at 126.5°, the boiling-point given by L'Hôte. By decomposing with water pure vanadic acid was obtained, which was carefully dried.

Preparation of Crude Vanadium.—Vanadic anhydride was mixed with finely pulverized sugar carbon in the following proportions:

	Grams.
Vanadic anhydride	182
Sugar carbon	60

Three hundred grams of this mixture were heated in the electric furnace with a current of 900 amperes at 50 volts. The length of the experiment was five minutes. A highly carbonized vanadium was obtained which, on analysis, gave the following figures:

	1.	2.	3.	4.	5.
Carbon	10.5	13.8	11.6	16.2	15.9

In another series of experiments we used vanadic anhydride (100 parts) and carbon (20 parts) and obtained fusions which contained:

	1.	2.	3.
Carbon	9.9	9.2	9.83

All of these experiments were made in carbon tubes. It was necessary to employ an intense current for a very short time, since the anhydride fuses easily and adheres to the tube, in which case it carbonized rapidly.

When we tried to refine the crude vanadium all our attempts were fruitless on account of the ready liquefication of the vanadic acid. The work of Roscoe has demonstrated that the preparation of vanadium is one of the most difficult in inorganic chemistry.

The strong affinity of vanadium for nitrogen seems to increase the difficulties. It is necessary to heat to a very high temperature in order to destroy the nitride.

[1] L'Hôte: *Ann. chim. phys.*, 6e série, **22**, 407 (1891).

By heating pure vanadic acid for two minutes in a carbon tube, with a current of 1000 amperes at 60 volts, and by taking care to have an atmosphere of hydrogen in the tube, we were able to obtain vanadium which contained only 5.3 to 4.4 per cent. of carbon. Another sample heated three minutes contained 7.42 per cent. carbon.

Properties of Crude Vanadium.—Vanadium containing 5 per cent. of carbon has a white color, a bright, metallic fracture, does not oxidize in the air and has a density of 5.8 at 20°. Roscoe found 5.5 as the density of vanadium, which contained traces of oxygen and 1.3 per cent. of hydrogen. Crude vanadium takes fire at redness in oxygen. Chlorine attacks it at dull redness without evolution of light. Nitrogen readily combines with it and, in general, this vanadium is more easily attacked by acids than the definite carbide of which we shall speak later. Hydrochloric acid does not attack it either cold or hot, while boiling concentrated sulphuric acid attacks it very slowly; as its other properties are similar to those of the vanadium of Roscoe, we will pass on.

Preparation of Vanadium Carbide.—When vanadic anhydride mixed with sugar carbon is heated in a carbon tube in the electric furnace for nine or ten minutes, with a current of 900 amperes at 50 volts, a metallic fusion of a definite carbide of vanadium is obtained, which at the moment of solidification deposits a small quantity of graphite.[1]

Properties of Vanadium Carbide.—Vanadium carbide, VC, is volatile when strongly heated in the electric furnace. Its melting-point is a little higher than that of molybdenum. In the liquid condition it has a metallic appearance. Its density is 5.36 and it scratches quartz with ease. It appears in well-formed crystals. Chlorine attacks it above 500° with evolution of light and gives a readily volatile, liquid chloride. It burns in oxygen at dull redness with evolution of light. It does not combine with sulphur at the melting-point of glass. Nitrogen and ammonia attack it at redness with formation of the nitride. At dull redness it does not

[1] In an experiment made in a crucible, a piece of lime, from the arch of the furnace, fell into the crucible, and formed a mixture of vanadium carbide and calcium carbide. This compound is not permanent in the air and gives vanadium carbide which appears in distinct isolated crystals. The excess of lime was removed by acetic acid and the dry mixture treated with methylene iodide to effect the removal of some crystals of graphite, by difference in density.

act on hydrochloric acid gas, water vapor or hydrogen sulphide. Hydrochloric and sulphuric acids do not attack it, while it reacts with nitric acid in the cold.

Oxidizing agents, such as fused potassium nitrate and chlorate, decompose it at dull redness. With the chlorate, light is evolved.

Analysis.—Vanadium carbide, on analysis, gave the following results:

	1.	2.	Theoretical for VC.
Carbon	18.39	18.42	18.98
Vanadium	81.26	80.79	81.01

Alloys of Vanadium.—Notwithstanding its high melting-point, vanadium readily forms alloys. We studied some of them. When a mixture of iron oxide, vanadic anhydride, and sugar carbon, in the proportion to form an alloy containing 20 per cent. of vanadium, is heated for three minutes in the electric furnace with a current of 900 amperes at 50 volts, there is obtained a homogeneous fusion, gray-white in color and having a crystalline fracture. The alloy is brittle, but can be filed. It contained:

Iron	72.96
Vanadium	18.16
Carbon	8.35

A mixture of vanadic anhydride, copper oxide and carbon, in the ratio to form an alloy containing 5 per cent. of vanadium gave, under the same conditions in the electric furnace, a well-fused mass of a bronze color which was very malleable, could be easily filed and was harder than copper. It contained:

Copper	96.52
Vanadium	3.38

It is possible to prepare an alloy of aluminum and vanadium by fusing aluminum in clay crucible, and throwing on its surface a mixture of vanadic acid and aluminum filings. The latter metal acts as a reducing agent; a bright light is produced, and on stirring the mass, a soft and malleable aluminum vanadium alloy is obtained, which can be filed. This alloy contained 2.5 per cent. of vanadium.

In another experiment we heated in the electric furnace a mixture of reduced silver with quantities of vanadic anhydride and carbon to form a 10 per cent. alloy. Length of heating, three minutes with 900 amperes at 50 volts. A metallic ingot was ob-

tained which was formed of two layers; the one was vanadium without a trace of silver, and below was silver with a pure white color which, after solution, gave no reaction for vanadium. These two elements are consequently without action on each other.

Conclusions.—By reducing vanadic acid with carbon in the electric furnace, it is possible to obtain readily and in large quantities a fusion of vanadium containing 4 to 5 per cent. of carbon. If it is heated very long, there is always obtained a definite and crystalline carbide having the formula VC. This compound does not act on water at the ordinary temperature and is more stable in presence of acids than the crude vanadium. At the temperature of the electric furnace, vanadium can unite with iron, copper and aluminum, while it does not form an alloy with silver.

In general, its properties are nearer those of the non-metals than of the metals; its carbide resembles titanium and zirconium carbides, which have similar formulas.

G. Zirconium

Fused zirconia is easily reduced by carbon in the electric furnace. If a large quantity of zircon is heated in a carbon crucible, after the action of the arc, there is found, under the fused zirconia, a button of metallic zirconium which contains neither carbon nor nitrogen, but does contain variable quantities of oxide.

On the other hand, by mixing zirconia with an excess of carbon a metallic-appearing body was obtained, having a bright fracture, containing no nitrogen, and which, on analysis, gave the following results:

	1.	2.	3.
Carbon	4.22	4.60	5.10

It is necessary to re-fuse this carbide in presence of an excess of liquid zirconia in order to refine it and obtain metallic zirconium. It is a very hard body, easily scratching glass and ruby. Its density has been found to be 4.25, which is very close to that of the zirconium of Troost, who has given 4.15 as the density of this element. Moreover, the properties of this metal have been very carefully studied by this investigator and we have nothing to add to the paper which he has published on this subject.[1]

Zirconium Carbide.—In connection with Lengfeld, we have

[1] Troost: "Recherches sur le zirconium," *Compt. rend.*, 61, 109 (1865).

studied a definite and crystalline compound of zirconium and carbon.

Preparation of the Zirconia.—The various methods heretofore described for obtaining pure zirconia present great difficulties when it is desired to work with a large quantity of zircon (zirconium silicate). We modified the preparation in the following manner: Picked zircon was reduced to powder, mixed with sugar carbon, and heated in the electric furnace for ten minutes with a current of 1000 amperes at 40 volts. Silicon, being much more volatile than zirconium as we have before shown, is vaporized in the beginning and there remains a well-fused metallic-appearing mass composed mainly of zirconium carbide which contains only a small quantity of silicon. This impure zirconium carbide is attacks at red heat by a current of chlorine. A mixture of zirconium, iron and silicon chlorides is formed. The quantity of silicon chloride was so small that no condensation of the liquid was noticed. These chlorides were treated with boiling concentrated hydrochloric acid, when quite pure zirconium chloride separated. It was collected and washed with concentrated hydrochloric acid, then dissolved in water, treated with hydrochloric acid, and evaporated to dryness. Care must be taken not to raise the temperature too high. The residue was taken up in distilled water and precipitated by ammonia. A completely white hydrate was obtained, which was quite free from iron and silicon. It was then roasted in the Perrot furnace.

The anhydrous zirconium oxide was mixed with sugar carbon and oil, pressed into cylinders, and heated. The mixture was placed in a carbon tube, closed at one end and heated for ten minutes in the electric furnace with a current of 1000 amperes at 50 volts. A portion of the zirconium volatilized at the beginning of the fusion. As is seen, the heat must be very strong, and it is only in the hottest part, that is, the bottom of the tube, that either a small button or metallic globules are found. It frequently happens that the carbon tubes cannot resist this high temperature; they are perforated or cracked, and zirconium carbide obtained under these conditions contains calcium carbide from the interior of the furnace, and it crumbles in the air. This reduction was made with the varying quantities of carbon and always gave the

same product. When the mixture was heated with a less-intense current, the carbide obtained contained nitrogen.

Properties.—Zirconium carbide has a gray color, metallic appearance and does not crumble in dry or moist air, even at 100°; it easily scratches glass, but is without action on the ruby.

The halogens readily attack the carbide; fluorine, in the cold, chlorine at 250° with evolution of light, bromine at 300° and iodine at 400°.

At dull redness it burns in oxygen with a bright light. Heated with sulphur, the latter is volatilized without forming a combination. At dull redness, in the vapor of sulphur, it gives a small quantity of sulphide.

Zirconium carbide, kept liquid in the electric furnace, dissolves carbon which it deposits, on cooling, as graphite. Water and ammonia are without action on it, either at the ordinary temperature or at dull redness.

Hydrochloric acid, dilute or concentrated, has no action even at the boiling-point. Dilute nitric acid slightly attacks it, but the concentrated acid acts violently on it if the temperature is raised. Concentrated sulphuric acid and aqua regia decompose it slowly in the cold, more rapidly in the warm.

Oxidizing agents, such as potassium nitrate, permanganate and chlorate energetically attack it; the chlorate gives an explosive reaction.

At its melting-point, potassium cyanide is without action, while fused potash dissolves it somewhat readily.

Analysis.—Estimation of the Zirconium.—The zirconium was estimated in the following manner:

(1) The carbide was attacked by fusion with a mixture of potassium nitrate and hydroxide. The fusion was taken up in water, hydrochloric acid added and the oxide precipitated with ammonia, ignited and weighed.

(2) The carbide was directly burned in a current of oxygen and the oxide of zirconium directly weighed.

Estimation of the Carbon.—The carbide was heated to redness in a current of chlorine and the residue weighed, giving the amorphous carbon. The residue not attacked consisted of pure graphite and the difference between its weight and that of the carbon gave

the weight of the combined carbon.[1] The results obtained were as follows:

	1.	2.	3.
Zirconium	83.00	82.8	86.1
Combined carbon	10.70	10.3	...
Graphite	6.00	8.76	...

By calculating without the graphite, the ratio of zirconium and combined carbon becomes:

	1.	2.	Calculated for ZrC.
Zirconium	88.6	88.7	88.3
Combined carbon	11.4	11.3	11.7

Conclusions.—Pure zirconia and carbon, when heated in the electric furnace outside of the arc, give zirconium carbide having the formula ZrC,[2] well crystallized and not decomposed by water between 0° and 100°. This fact is curious, since zirconium, in the classification of Mendeléeff, approaches thorium; its carbide is very stable, while the carbide of thorium decomposes cold water with formation of acetylene, ethylene, methane and hydrogen.

H. Titanium

Titanium is better known combined than in free condition. It has been obtained only in the form of an amorphous powder, whose appearance and properties have varied with each preparation.

In the first method, devised by Berzelius, potassium is made to act on an alkaline fluotitanate. Under these conditions a reddish powder is obtained which later has been shown to be only a nitride.

Wöhler[3] and later Wöhler and Deville,[4] causing sodium to act on potassium fluotitanate in a current of hydrogen, prepared another powder of a gray color, which they regarded as titanium, and which decomposed water at 100°.

[1] We attempted to estimate the combined carbon by treating the carbide with fuming nitric acid and passing the evolved gas over red-hot copper: the carbon dioxide was collected in a potash tube and weighed. The figures obtained were not concordant; organic compounds always appeared, which were only slowly destroyed by fuming nitric acid.

[2] We presented our first work on zirconium to the Academy of Sciences, May 29, 1893 (*Compt. rend.*, **116**, 1222). At the same session, Troost presented a study on the same subject and showed the existence of a carbide, ZrC_2, obtained with a current of low intensity (35 amperes at 70 volts), but operating in the arc.

[3] Wöhler: *Ann. chim. phys.*, 3e série, **29**, 166.

[4] Wöhler and Deville: *Ibid.*, 3e série, **52**, 92.

Recently Kern,[1] by action of the vapor of titanium chloride at redness in a current of hydrogen on sodium placed in a boat, obtained another powder which did not decompose water at 500°. Moreover, none of the authors of these works have given the analysis of the titanium which was always furnished by the reduction of a titanium compound with an alkali metal. The powerful affinity of titanium for nitrogen and the great difficulty of having a continuous current of hydrogen absolutely free from nitrogen greatly complicated this preparation. The specimens previously obtained all contained potassium or sodium, and silicon, oxygen, nitrogen and hydrogen.

Following our reduction of the oxide of uranium, silica and vanadic acid, by carbon in the electric furnace, we undertook the study of titanium.

When titanic acid in a crucible or in a carbon boat is heated in the electric furnace, with a current of 100 amperes at 50 volts (8-horse-power dynamo), a fused or crystalline indigo-blue titanium oxide is obtained. If the experiment is repeated with a current of 300 to 350 amperes at 70 volts (40-horse-power) a yellow, bronze-colored mass is obtained, partially fused. This is the titanium nitride, Ti_2N_2, of Friedel and Guérin.

In order to prepare titanium the temperature must be much higher. With a 45-horse-power dynamo, by varying the conditions of the experiment, we never obtained more than nitride. The preparation is impossible if the temperature is not above that of the decomposition point of titanium nitride.

When a mixture of titanic acid and carbon is heated in a carbon boat with an arc of 1200 amperes at 70 volts (by means of the electric furnace for tubes) a fused mass is obtained which, on cooling, has a distinct crystalline appearance and is composed of titanium carbide, TiC, entirely free from nitrogen.

When a mixture of titanic acid and carbon, without having the latter in excess, is heated in a crucible with the same arc, on cooling there is obtained a fusion whose upper portion, to a depth of 2 cm. to 3 cm., is fused and formed of crude titanium having a bright fracture and a varying content of carbon.

Under these conditions titanium nitride cannot exist, and only more or less carbonized titanium is present. These successive

[1] Kern: *Chem. News*, **33**, 57 (1876) and *Bull. Soc. Chim.*, **26**, 265 (1876).

actions of a more and more powerful arc, on a mixture of titanic acid and carbon, appear to be a decisive proof that the increase of temperature of the electric furnace is a function of the current. This study, by demonstrating that the powerful heat of the arc increases with the electrical intensity, increases the number of experiments to be undertaken in this direction.

Preparation of Titanium.—For titanic acid well-crystallized and carefully picked rutile from Limoge can be used. It contains only a small quantity of silica and iron. In this case the titanium obtained is not pure. It contains 1 to 2 per cent. iron and a little silicon.

Instead of the natural product, titanic acid prepared in the laboratory was substituted. This compound was intimately mixed with carbon, compressed and carefully dried. This mixture was packed into a cylindrical carbon crucible, 8 cm. in diameter, and placed in an electric furnace. Thirty to 40 grams were thus operated on. An arc of 1000 amperes at 60 volts was allowed to play for ten or twelve minutes; the current was interrupted, the apparatus allowed to cool and then the furnace was opened. The crucible contained a homogeneous mass which was liquefied only to a depth of a few centimeters. This material was covered with a yellowish layer of fused titanic acid.

If a current of 2200 amperes at 60 volts is used, the quantity of titanium obtained is greater, but the fusion of the entire mixture in the crucible is not complete. Each experiment gave about 200 grams of titanium. Under the fused titanium there was found a layer of more or less crystalline, yellow nitride and on the bottom of the crucible another layer of blue titanium oxide bristling with little crystals. These layers of various composition are a proof of the rapid lowering of the temperature from the surface to the bottom of the crucible.

The fusion of titanium obtained under these conditions is more or less rich in carbon, according to the proportion of titanic acid and carbon. We obtained the following results:

	Amperes.	Volts.	Length of heating. Min.	Carbon. Per cent.	Ash. Per cent.
Rutile and carbon	1000	70	15′	15.3	3.3
" " "	1200	70	12′	11.2	2.0
" " "	1000	60	12′	8.2	2.4
Titanic acid and carbon	1100	70	10′	7.7	4.5
Titanium carbide and titanic acid	2000	60	9′	4.8	2.1

This fusion of titanium can be mixed with titanic acid, then heated again in the electric furnace with an arc as intense as before. Under these conditions, especially if care is taken to work rapidly in order to avoid the carbonizing action of the arc, a titanium containing neither nitrogen nor silicon is obtained, and only containing as impurity about 2 per cent. of carbon. Heretofore it has not been possible to obtain so low a content.

Properties.—Titanium, prepared under these conditions, appears as a fused mass, with a bright white fracture, hard enough to scratch quartz and steel, yet brittle and can easily be reduced to powder in a steel and then in an agate mortar. Its density is 4.87.

Chlorine attacks titanium at 350° with evolution of light, forming the liquid chloride $TiCl_4$. Bromine at 360° gives a dark-colored bromide. Iodine acts at a still higher temperature without evolution of light, giving solid titanium iodide, which has been prepared in a pure state by Hautefeuille. In oxygen, titanium burns with light at 610°, leaving a residue of amorphous titanic acid. Sulphur slowly attacks titanium at the point of the softening of glass. A dark-colored body is formed which is not attacked in the cold by hydrochloric acid and evolves hydrogen sulphide with concentrated and boiling acid.

In a current of nitrogen, titanium is converted into nitride at 800°. The combination takes place with evolution of heat and the boat is carried to a higher temperature than that of the tube. This is the first good example of the combustion of an element in nitrogen.

The vapor of phosphorus reacts about 1000°, giving a dark phosphide, but the action is only superficial. Carbon dissolves in fused titanium and combines to form a definite carbide. The excess of carbon in solution subsequently crystallizes as graphite.

In the electric furnace, silicon and boron unite with titanium to give the fused or crystalline borides and silicides, which have as great hardness as the diamond.

Titanium readily dissolves in fused iron, and the alloy obtained can be easily filed. It also dissolves in lead. With copper, tin and chromium it gives alloys which we will study further.

Hydrochloric acid, concentrated and boiling, slowly attacks titanium with evolution of hydrogen, and gives a violet solution.

With warm nitric acid the action is somewhat slow, and titanic acid is formed with aqua regia; solution is much more rapid, but the titanic acid, which is formed, retards the reaction.

Dilute sulphuric acid dissolves titanium more readily; it also acts in the cold, but in order to have continuous action it is necessary to raise the temperature. Hydrogen is evolved and the solution takes on a violet color. With concentrated and boiling sulphuric acid, sulphurous acid is formed.

In a mixture of nitric and hydrofluoric acids the titanium dissolves with a violent effervescence. The action is as rapid as with silicon.

Oxidizing agents react on titanium energetically. Fused potassium nitrate atacks it without apparent evolution of heat, but if powdered titanium is thrown into potassium chlorate heated to its temperature of decomposition, it takes fire. The alkaline carbonates attack it with evolution of light. The same is true with a mixture of potassium nitrate and carbonate. Powdered titanium, heated in a current of water vapor, does not begin to decompose this gas until at about 700° and it is scarcely at 800° that regular decomposition is produced. Titanic acid is formed and hydrogen is obtained.

Silver fluoride is reduced at 320° by powdered titanium, with evolution of light.

Analysis.—Titanium, reduced to powder, was attacked by a fusion mixture of 2 parts carbonate and 8 parts nitrate of potassium. The white mass obtained was taken up in cold water; the residue of insoluble titanate dissolved in cold hydrochloric acid and was added to the first solution. The titanic acid was precipitated by ammonia with the necessary precautions.

To determine the carbon, the titanium was heated to dull redness in a current of pure, dry hydrochloric acid and by combustion of the black residue in oxygen, the weights of the carbon dioxide and ash were obtained. These analyses gave the following results:

	1.	2.	3.
Titanium	94.80	96.11	96.69
Carbon	3.81	2.82	1.91
Ash	0.60	0.92	0.41

Titanium Carbide, TiC.—When a mixture of 160 parts of titanic acid and 70 parts of carbon is heated for ten minutes with

an arc of 1000 amperes at 70 volts, a definite carbide is obtained according to the equation

$$TiO_2 + 3C = TiC + 2CO.$$

This titanium carbide appears in fused lumps, having a bright fracture, or as a mass of crystals; it contains a slight excess of carbon which has crystallized as graphite. This graphite energetically retains titanium and on combustion in oxygen leaves a yellow-white ash in which titanic acid can be easily recognized.

Titanium carbide has a density of 4.25. It is not attacked by hydrochloric acid, which in some cases permits the ready separation from an excess of titanium. Aqua regia dissolves it slowly. At 700° water vapor has no action on it. Its other reactions are similar to those of titanium. It burns much better, however, in oxygen than does titanium. At low redness it takes fire in the gas and evolves sufficient heat to raise the material to a white heat. Reduced to powder and thrown into the flame of a burner, it gives beautiful sparks, much more brilliant than those given by titanium.

Analysis:

	1.	2.	3.	Theoretical for TiC.
Carbon	20.06	19.40	19.18	19.36
Titanium	....	79.94	80.41	80.64

Titanium Nitride.—The nitride obtained by heating titanic acid either with addition of carbon or only under the action of an arc of 300 amperes at 70 volts, appears as a bronze-colored, fused mass, difficult to break, very hard, scratching the ruby and slowly cutting the diamond. Its density is 5.18.

On analysis it gave 78.3 to 78.7 per cent. of titanium. This compound, free from carbon, corresponds to the nitride described by Friedel and Guérin, whose density was 5.28 and whose content of titanium was 78.1 per cent.

Titanium Oxide.—The blue oxide obtained by the action of the electric arc on titanic acid, when this arc is of feeble intensity, resembles in appearance titanium protoxide whose existence is still doubtful, and which has been mentioned by Laugier and Karsten. The oxide that we obtained presented the appearance of a dark indigo-blue mass, covered and formed of a mass of crystals.

Conclusions.—When the heat produced by an electric arc,

whose intensity is variable, is made to act on a mixture of titanic acid and carbon, there is obtained:

(1) Blue protoxide of titanium;

(2) Fused titanium nitride, Ti_2N_2;

(3) Fused titanium or a crystalline carbide, TiC.

Fused titanium is the most refractory body that we obtained in the electric furnace; it is more infusible than vanadium. It is more so than such metals as pure chromium, tungsten, molybdenum and zirconium. It can be prepared in the electric furnace only at a temperature above that of the decomposition of its nitride and by means of the arc from a 100-horse-power dynamo. Fused titanium on the other hand has a less affinity for nitrogen than the powder obtained by the action of the alkaline metals on the fluotitanates, while titanum, reduced to powder, burns in nitrogen at a temperature of 800°. As a whole, the properties of titanium resemble those of the non-metals, and silicon in particular.

I. Silicon

We have previously shown that silica was readily volatilized in the electric furnace. By using a current of 1000 amperes at 50 volts, the formation of the vapor of silica is very abundant. In a few moments it surrounds one with very light filaments of silica which hover in the air and remain for a long time in suspension. If these filaments are examined under the microscope it is seen that they are formed of very small spheres of silica, which in water show a very pronounced Brownien movement. When the experiment is stopped without completely volatilizing the silica, the part which remains in the crucible sometimes shows, on the lower portion, characteristic crystals of silicon, such as have been described by Senarmont. This experiment showed that silica can be reduced at a high temperature by carbon.

By heating, in the electric furnace, a mixture of quartz crystals and powdered carbon, in a carbon cylinder closed at one end, the phenomenon is much more distinct. The aperture of the tube is covered with flocculent silica; below are found very clear, almost colorless, crystals of carbon silicide and a little lower a ring of bright black crystals mixed with fused globules;[1] these black crystals were attacked only by a mixture of nitric and hydrofluoric

[1] Some of these globules of silicon contained small, quite transparent crystals of carbon silicide, having a beautiful yellow color.

acids. They took fire in the cold in fluorine and burned brightly, giving silicon fluoride. Some showed distinctly the appearance of the superimposed crystals obtained by solution in fused zinc. They were always mixed with carbon silicide, but the crystalline powder, collected from the entire tube, contained 20 to 30 per cent. of crystalline silicon. The experiment which we repeated many times shows that under the action of the electric arc, silica is reduced by carbon, giving silicon. When the temperature is not very high, a part of the silicon escapes the action of the carbon and is found as crystals or fused globules.

By cooling the vapor of silicon at the moment of its formation, this proceeding can be used to prepare silicon.

Vigouroux, using our electric furnace, has shown that liquid silica can easily be reduced by aluminum, giving a good yield of crystalline silicon.

J. Aluminum

Aluminum formerly was regarded as an oxide which could not be reduced, but such is not now the case. If perfectly transparent crystals of corundum, introduced into a boat placed in a carbon tube in the electric furnace, are heated with a current of 1200 amperes at 80 volts, the alumina is volatilized in a few moments. In our experiments, the boat which was completely converted into graphite did not contain a trace of ash, and on each side of the tube was found a crystalline layer of graphite and alumina, containing spheres 2 mm. to 3 mm. in diameter, of metallic aluminum which could be easily recognized.

This experiment was varied by using a carbon tube closed at one end, which was introduced into the electric furnace in such a manner that the closed portion was carried to the maximum temperature. The tube measured 0.40 meter long, and 40 mm. internal diameter. At the bottom of this apparatus 100 grams of alumina were placed and heated for fifteen minutes with a current of 300 amperes at 65 volts. At the end of the experiment, copious vapors were evolved from the end of the tube, and these vapors condensed on a cold body gave a white deposit of alumina.

This substance treated in the cold with dilute acetic acid, which removed traces of iron and lime, then washed with distilled water and dried, showed in the center of the irregular masses small spheres of fused alumina.

After cooling, a white deposit of alumina was found in the upper portion of the tube while in the lower portion was found a mass of fused alumina which had a different appearance depending on whether the parts had been more or less highly heated.

The portion which had been carried to the highest temperature was covered with a film of graphite from the condensation of the vapor of carbon which filled the tube. On the wall were observed small, white or slightly yellow globules which were formed of a mixture of aluminum and the carbide of the metal.

The reaction becomes more and more conclusive if, under the same conditions, there is heated an intimate mixture of alumina and starch which, on decomposing, gives the carbon necessary for the reduction.

In an experiment that lasted eighteen minutes (300 amperes at 65 volts) some aluminum was obtained, containing beautiful leaves of the carbide, Al_4C_3, which we will describe later. The experiment was repeated four times and the results were always the same; and each time also the cold mixture was covered with graphite from the condensation of the vapor of carbon.

Another series of experiments made in crucibles, at a lower temperature, showed that alumina can be fused and kept in the liquid state in a carbon crucible without reduction. In an experiment made in a tube closed at one end, it happened that the other end of the cylinder became closed by a plug of alumina and carbon. This experiment, which was not so long as the preceding on account of the formation of a short-circuit, showed in the heated portion a layer of graphite and small hexagonal crystals, showing the phenomenon of iridescence, and entirely formed of alumina. The tube contained no trace of metallic aluminum. The production of the mixture of corundum and crystalline graphite shows that the vapor of alumina, which is easily formed, and the vapor of carbon can come in contact without producing aluminum. A much higher temperature is necessary for the vapor of carbon to reduce the vapor of alumina. Therefore, alumina is not reduced in the electric furnace by carbon, but reduction takes place when the vapors of the two bodies are carried to a very high temperature. In this case alumina loses its oxygen and gives metallic aluminum which is partially carbonized.

Impurities of Aluminum.[1]—The previous work as well as the discovery of a crystalline aluminum carbide, which we will describe later, has introduced the analytical study of the aluminum prepared by electrolysis.

The aluminum industry, founded in France by Henri Sainte-Claire Deville in 1854, has progressed very rapidly. Since this metal has been obtained by the decomposition of alumina with strong electric currents, its preparation has become so practical that its price has descended to 4 francs per kilogram. The rapid progress of this industry causes the hope that the price will be still further lowered.

It is probable that the qualities of this light metal will then afford even more numerous applications than at present. The secondary points which demand further investigation, such as the refining of aluminum or the preparation at a cheap price of pure aluminum from bauxite or kaolin, without doubt, will soon be solved. The aluminum industry has already some outlets. Outside of its use in the refining of steel and cast iron[2] its alloys show very curious properties. The different experimenters who have studied the properties of aluminum have frequently found contradictory results. The same has been true when, on account of its lightness, some countries have attempted to use it in the manufacture of small articles of equipment such as plates, cans and pans with the view of lightening the weight of knapsacks of foot soldiers. While this metal is useful and possesses the qualities which have caused its use to be worthy of praise, it has, on the contrary, caused deceptions.

These difficulties appear to be particularly due to the difference in the composition of commercial aluminum. We would add that the aluminum produced by the different electrolytic methods is never pure and that its composition is somewhat variable; all metallurgists know how the chemical and physical properties of a metal vary with traces of foreign bodies. It will then be interesting to industry to endeavor to obtain aluminum as pure as possible, whose properties will be constant and always give the same results.

[1] *Compt. rend.*, July 2, 1894, **119**, 12.

[2] This refining of steel has been studied in England by Hadfield and in France by Le Verrier.

The impurities of technical aluminum already known are two in number: Iron and silicon.

The iron comes from the minerals, the electrodes and the crucibles. The purity of the alumina and the careful manufacture of the electrodes and crucibles should remove this. Minet has published interesting experiments on this subject and has shown what troublesome influence could be exerted by a small quantity of iron.

The silicon also comes partly from the electrodes and the crucibles, but particularly from the alumina used. It appears very difficult to avoid the presence of this non-metal. Although in certain cases these elements have no injurious action, we have been able to decrease their quantity by a simple fusion of the metal under a layer of alkaline fluoride.[1] But, besides the silicon and the iron, there exist in technical aluminum two other impurities which have not heretofore been noted. We refer to nitrogen and carbon.

On treating a piece of commercial aluminum with a 10 per cent. solution of potash, the metal is rapidly attacked and the hydrogen which is evolved in large quantities contains a small quantity of ammoniacal vapors. This can be shown by passing the hydrogen through bulbs containing Nessler's reagent. A coloration soon appears and finally a precipitate. It is necessary to use absolutely pure potash for this reaction. On passing a current of nitrogen into fused aluminum and saturating it with this gas, the metal obtained showed a slight decrease in its tensile strength and in its elongation. The presence of nitrogen can thus vary the physical properties of aluminum.[2]

Mallet, of the University of Virginia, showed in 1876 the existence of aluminum nitride; it is slightly soluble in aluminum and to it can be attributed this change of properties.[3]

[1] The specimen of aluminum that we used in this work had the following composition:

Aluminum	98.02
Iron	0.90
Silicon	0.81
Carbon	0.08
Nitrogen	trace

After a fusion under a layer of the alkaline fluorides, it contained only 0.57 per cent. of silicon.

[2]

	Elastic limit. Kilograms.	Breaking strength. Kilograms.	Elongation. mm.
Fused aluminum	7.500	11.102	9
Aluminum saturated with nitrogen	6.500	9.600	6

[3] Mallet: "Nitride of Aluminum," *J. Chem. Soc.*, **30**, 349 (1876).

We constantly found carbon in commercial aluminum and in much larger quantity than nitrogen. On treating 100 grams of aluminum with a current of hydrochloric acid or hydriodic acid gas free from oxygen, a gray residue remained. This substance, treated with dilute hydrochloric acid, gave a light amorphous carbon, brown in color, which completely burned in oxygen, giving carbon dioxide; this carbon contained no graphite. This carbon can be weighed by treating 10 grams of aluminum with a concentrated potash solution. The residue is taken up in water, and dried and burned in a current of oxygen. From the weight of the carbon dioxide collected, the weight of the carbon is readily deduced. We thus found the following figures: Per cent. of carbon, 0.104, 0.108 and 0.080. The action exerted by this element on the physical properties of aluminum appears to be very characteristic.

To make it more evident we fused aluminum of good quality in a crucible; we cast a portion in an ingot mold; then in the part still remaining liquid, we dissolved crystalline aluminum carbide prepared in the electric furnace. A few moments later we cast another sample of metal and thus obtained two samples, one fused aluminum, the other carbonized aluminum.

These ingots were tested and, while fused aluminum showed for one square millimeter a breaking strength of 11.000 kilograms and an elongation per 100 of 9 mm., carbonized aluminum showed only a breaking strength of between 8.600 kilograms and 6.500 kilograms and an elongation of 3 mm. to 5 mm. per 100.[1]

Having had occasion to make analyses of aluminum from the three very large manufacturers in La Praz (France), Neuhausen (Switzerland) and Pittsburg (United States), we found another impurity which appears to be of great importance from the standpoint of preservation of the metal. We allude to the presence of sodium. The presence of sodium in an aluminum can be detected in the following manner: 250 grams of carefully prepared aluminum filings are introduced into an aluminum flask with 300

[1] These experiments were made on metal which had been fused without rolling or heating.

After one rolling without annealing, we obtained as follows:

	Elastic limit. Kilograms.	Breaking strength. Kilograms.	Elongation. mm.
Carbonized aluminum	20.00	20.793	2.5
After rolling and annealing	7.700	13.000	26.5

cc. of distilled water which has been prepared in a metallic apparatus. The mixture is left in contact for two weeks, being heated to boiling every day. It is then brought on to a filter.[1] It is washed with boiling water and the liquid obtained, which is slightly alkaline, is evaporated to dryness in a platinum dish. The residue is heated to low redness, the mass turns brown, and pure dilute hydrochloric acid is added, when carbon dioxide is evolved. It is again evaporated to dryness, heated to about 300° to drive off the excess of carbon dioxide, and a residue is obtained which shows all the characteristics of sodium chloride. This is taken up in water and the chlorine determined as silver chloride; from the weight of the latter the quantity of sodium extracted by the action of the water on the aluminum filings, is deduced.

In making a complete analysis of the metal, we found sodium in a number of specimens of aluminum. The content varied from 0.1 per cent. to 0.3 per cent. An old aluminum prepared by the firm of Bernard contained 0.42 per cent.[2]

When an aluminum contains a small quantity of sodium, it is first slowly attacked by cold water, then the action increases. In fact, if a small quantity of water is added, and not renewed with such a sheet of aluminum, a thin layer of alumina forms on the metal. After many days the liquid gives a distinct alkaline reaction to litmus paper. From this point the decomposition becomes more rapid. In all cases where aluminum contains sodium, a little alkali is formed which reacts on the metal to give aluminate. This sodium aluminate is subsequently dissociated by water with deposition of alumina and formation of soda, and when the liquid is slightly alkaline, it is evident that the decomposition becomes much more active.

The alloys which can be prepared with aluminum have, therefore, entirely different properties, according to whether they contain or do not contain a small quantity of sodium.[3]

[1] In this experiment a small quantity of soluble alumina is frequently obtained similar, without doubt, to the colloidal alumina which passes through the filter and which subsequently precipitates.

[2] The presence of sodium in commercial aluminum shows that the electrolysis of a mixture of cryolite and alumina gives rise to a number of secondary reactions in which the sodium can play a part depending on the composition of the bath and the intensity of the current.

[3] It is therefore necessary, in all the investigations made on this subject, to determine the exact composition of the aluminum used.

It is for this reason that in a study on the alloys of aluminum and tin, Riche has shown that these alloys decompose water at the ordinary temperature.[1] I have been able to prepare an alloy of 6 per cent. of tin with aluminum quite free from sodium, and after remaining for two months in ordinary water the metal was spotted in many places, giving small efflorescences of alumina, but there was no evolution of gas. The experiment was made as follows: Aluminum free from sodium was alloyed with 6 per cent. of tin, avoiding the action of nitrogen and the furnace gases, since Franck has shown that aluminum at redness decomposes carbon dioxide and as well carbon monoxide. An alloy was thus obtained which, rolled under strong pressure, gave:

	Annealed.	Hard-drawn.
Resistance	17.6	28.43
Elasticity	8.20	22.90
Elongation	20.0	6.0

A sheet of this metal was divided into two parts: The first was placed in the water of the Seine and for days was kept in agitation; the second was placed in a Bohemian glass vessel in Seine water, on top of which was introduced a layer of several centimeters of oil. The mean temperature of the laboratory was about 20°. The experiment began the 30th of September and lasted for two months. During this time the aluminum became covered with a white efflorescence; it was indented on nearly all of its surface, but in the two cases there was no evolution of a bubble of hydrogen. That which was placed in the water which was agitated daily was more rapidly attacked. This experiment was only made with an alloy containing a small amount of tin. Riche has shown that for higher contents of tin the decomposition of the water becomes active and has thus shown the reason why attempts to solder aluminum with an alloy having a base of tin should not be made. Moreover, aluminum is a metal which, when carefully annealed, is easily worked by stamping and by rolling, but there should not be demanded for it that which it cannot do.

Riche, to whom I have communicated these experiments before publication, has also observed the presence of sodium in some samples of aluminum.

[1] Riche: "Recherches sur les alliages de l'aluminum," *Journal de pharmacie et de chimie*, 6e série, **1**, 5 (1895).

Moisonnier, principal pharmacist in the military hospital of Saint-Martin, who has undertaken lengthy observations on this subject, found the same with a sample of alumina containing 0.4 per cent. of sodium.

Another important point to which we call attention in connection with the alloys of aluminum, and in particular those with copper, is that non-homogeneous alloys are very difficult to preserve.

In his work on the equivalent of aluminum, Dumas has shown the non-homogeneity of the alloy prepared according to the method of Deville.[1] We frequently had the opportunity to ascertain on objects of stamped aluminum the bad effect of this lack of uniformity. When distilled water is allowed to remain in such a vessel, after fourteen days there were formed small, white spots of hydrated alumina; the spots were surrounded by bright circles which continued to grow. If, after having separated the attacked portion, the aluminum hydroxide was removed, there was frequently seen, under the microscope, a small particle of carbon or other substance which had formed a galvanic element and which had effected the metal over a more or less large surface. If instead of allowing water to remain on the non-homogeneous aluminum, a saturated solution of sodium chloride is substituted the phenomenon is increased, and each particle of carbon gives an action sufficiently great to pierce the metal. This formation of the elements of a battery on the surface of the aluminum is the cause of the alteration of the metal.

On the contrary, with a quite homogeneous metal containing neither nitrogen, carbon nor sodium, no point of attack is produced and the water which remains on the metal preserves its clearness and contains no alumina.

The same phenomenon is presented with alcohol diluted with water, rum for example, and in the case of aluminum of poor quality, it explains the action on canteens, an action which sometimes proceeds with great energy.[2]

[1] Dumas: I know, therefore, that in impure aluminum the distribution of the iron and the silicon is not uniform," "Mémoires sur les equivalents des corps simples," *Ann. chim. phys.*, 3e série, **55**, 153.

[2] Drs. Plage and Lebin, in the experiments which were undertaken in the laboratory of the Friedrich Wilhelms-Universität in Berlin, attributed this action on aluminum canteens and cooking utensils to tannin, Berlin, 1893.

Since aluminum has a great tendency to form an electric couple with other metals, it should be used only alone. A particle of iron or brass in contact with aluminum in a short time always causes oxidation of the metal and its transformation into alumina. All of the manufactories which have put in use large surfaces of aluminum have found, by experience and to their cost, the truth of this decomposition. Commercial aluminum contains, besides iron and silicon, a small quantity of carbon, traces of nitrogen,[1] and sometimes sodium. These different substances considerably modify the properties of the aluminum, but it is hoped that electro-metallurgy will soon produce a purer metal and one of constant composition.

We have not called attention in this work, made from the chemical standpoint, to the importance of reheating in the rolling and stamping of aluminum. It is known that without this precaution the metal cracks and becomes useless.

NEW METHOD FOR THE PREPARATION OF ALUMINUM ALLOYS.[2]

The method of preparation which we have indicated for the alloy of aluminum and vanadium from vanadic acid can be applied to a number of oxides. It is based on the powerful affinity of aluminum for oxygen. The work of Winkler and others has shown the ease with which certain oxygen compounds can be reduced by magnesium. Aluminum can also be used in such cases. In utilizing this property I have been able to obtain aluminum alloys with most of the refractory metals which I have obtained, by reduction in the electric furnace.

The preparation of these alloys is simple. It consists in throwing on a bath of liquid aluminum, a mixture of the oxide to be reduced, and aluminum filings.

The combustion of a part of the aluminum by the atmospheric air at the surface of the bath evolves so much heat that the most refractory oxides are reduced. The metal then passes continuously into the bath of aluminum and raises the melting-point of the alloy. This preparation is made in the dry way without addition

[1] We also add that commercial aluminum often contains a small quantity of alumina having no crystalline form. In some samples we found, with the microscope, in the residue from the treatment with dilute hydrochloric acid, small, clear crystals of carbon boride The boron of this compound comes from the boric acid which has served as the binding material for the carbon of the electrodes.

[2] *Compt. rend.*, No. 23, June 8, 1896, **122**, 1302.

of a flux. I have thus been able to obtain alloys of aluminum with nickel, molybdenum, tungsten, uranium and titanium. It frequently happens that the heat evolved by the reaction is so great that the eye cannot stand the light. Many times we prepared alloys of 75 per cent. titanium which have been kept in the liquid state by this great evolution of heat. Alloys of 10 per cent. are easily obtained. It should not be forgotten that the reaction is sometimes explosive. These alloys present some interesting features. They allow, in fact, the introduction of refractory metals, whose melting-point is higher than the temperature of our ordinary furnaces, into a metal whose melting-point is lower.

When, for example, metallic chromium is brought into contact with melted copper, the latter only dissolves a small quantity about 0.5 per cent., and it is impossible to introduce more. If an alloy of aluminum and chromium is used, it dissolves in all proportions in melted copper, giving a mixed alloy containing copper, chromium and aluminum. In this mixed alloy it is easy to eliminate the aluminum by covering the fused bath with a thin layer of copper oxide. The latter easily dissolves in the copper and burns the aluminum which then floats on the surface of the bath as alumina. This proceeding similarly, can serve to introduce tungsten or titanium into a bath of steel kept melted in a Martin-Siemens furnace. We consider this method general and that it will permit of the preparation of a large number of new alloys.

Analyses of Aluminum and Its Alloys.[1]—Since the impurities which we find in the commercial aluminum greatly modify its properties, it is necessary to make as exact an analysis as possible. The methods heretofore used in industry often leave much to be desired. Either the ferruginous residue which the aluminum leaves on treatment with dilute hydrochloric acid is regarded as silicon, or the aluminum is estimated by difference.

Preliminary Work.—It should first be determined if the aluminum contains copper. A small quantity of the aluminum (about 2 grams) is dissolved in hydrochloric acid, diluted with water, and this solution is treated with a current of hydrogen sulphide. When the content of copper is very slight, it is well to gently warm the solution and to keep it lukewarm for several hours after passing in the hydrogen sulphide. It is filtered and the copper

[1] *Compt. rend.*, December 9, 1895, **121**, 851.

is tested for, qualitatively in the residue. A qualitative analysis is then made to establish the presence of silicon, iron, carbon, nitrogen, titanium and sulphur.[1]

1. Aluminum Containing no Copper.—*Estimation of Silicon.*—About 3 grams of the metal are weighed off and treated with pure hydrochloric acid, diluted 1 to 10, when a gray-colored residue remains (containing silicon, iron, aluminum and carbon). The powder is separated and fused with a small quantity of sodium carbonate in a platinum crucible. The contents of the crucible are taken up in dilute hydrochloric acid, and this solution added to the first. The liquid is brought into a porcelain dish and evaporated to dryness on the water-bath. The dish is placed in an air-bath and heated to 125°. The residue should be perfectly white, pulverulent and should not be attached to the stirring rod. To this end it is well to scrape the sides of the dish with a spatula, and to crush the lumps which have formed with an agate pestle. The dish is allowed to remain for twelve hours in the hot air-bath until a glass stirring rod moistened with ammonia, held over the residue, no longer gives white fumes, showing that the hydrochloric acid has ceased to come off. The drying being completed, the residue is taken up in lukewarm distilled water to which is added a small quantity of hydrochloric acid. The liquid is then boiled for several minutes, the silica remains insoluble and is filtered off. After washing and drying, it is ignited and weighed.[2]

Estimation of the Aluminum and Iron.—The first solution of the aluminum in hydrochloric acid 1 to 10, after the separation of the silica, is diluted with water to a volume of 500 cc., 50 cc. of this solution, corresponding to 0.150 gram of aluminum, are taken, neutralized in the cold with ammonia and the two oxides are precipitated with recently prepared ammonium sulphide. The mixture is allowed to digest for an hour. The precipitate is then thrown on a filter, washed, dried, ignited and weighed.

We have not used ammonia for this precipitation, since, in order to be complete, the solution must not be too dilute and should contain a somewhat large quantity of ammonium salts and very

[1] We have previously shown how it is possible to detect the presence of nitrogen in aluminum. "Impuretés de l'aluminium industrie," *Compt. rend.*, **119**, 12 (1894).

[2] In order to be sure that this silica does not contain alumina or iron oxide, pure hydrofluoric acid is added to the platinum crucible which was used in the ignition. After evaporation to dryness on a sand-bath, no residue should remain.

little free ammonia. It is true that the excess of ammonia can be expelled by boiling, but the boiling should be stopped while the liquid is still slightly alkaline; if this point is passed, the alumina slowly reacts on the ammonium salt in solution and the liquid becomes acid. On account of these minor difficulties we preferred the precipitation by ammonium sulphide.

As is known, precipitated alumina is very difficult to wash. It should be done by decantation in a beaker of Bohemian glass, and with boiling water. The washing is complete when the wash-water no longer contains chlorine. The precipitate is thrown on a filter, dried, ignited and weighed. The weight of the alumina and iron sesquioxide contained in the aluminum is thus obtained. The iron, at first precipitated as sulphide, rapidly oxidizes by the washing and the ignition. It is also necessary to carefully dry the alumina before heating to redness. The ignition should be made slowly, since the dried alumina sometimes decrepitates when it is strongly heated. Finally, the ignition should be continued long enough, as alumina only completely loses the water which it contains, at a high temperature.

Estimation of the Iron.—To estimate the iron, 250 cc. of the first solution are taken after separation of the silica. This solution is reduced by evaporation to about 100 cc. Caustic potash free from silica,[1] is added, which precipitates at first the iron and alumina and since the potash is in excess, the alumina dissolves.

The mixture is kept for ten minutes near the boiling temperature. The precipitate is washed five or six times by decantation with boiling water, then thrown on a filter. The precipitate is dissolved in dilute hydrochloric acid, and precipitated by an excess of caustic potash. After washing and filtering, it is again dissolved in hydrochloric acid, and this time the iron is precipitated by ammonia. The precipitate is thrown on a filter, washed, ignited and weighed as iron sesquioxide. From the weight of the two oxides obtained in the preceding operations, the weight of iron oxide is subtracted, the difference being the alumina.

Estimation of the Sodium.—This method of analysis is based on the fact that aluminum nitrate is destroyed by heat, giving alumina at a temperature below that of the decomposition of sodium nitrate. Five grams of aluminum (whether containing

[1] It is necessary to be certain that the potash contains no silica.

copper or not) in filings or strips are dissolved in a conical vessel in nitric acid,[1] diluted with its volume of water and at a moderate temperature. The reaction does not take place in the cold, and the temperature must be carefully raised, since the heat evolved in the reaction can become great enough to occasion a violent evolution of gas. The solution is concentrated in a platinum dish on the water-bath, then evaporated to dryness on a sand-bath or over a free flame; the residue is reduced to a powder with an agate pestle. It is then heated to a temperature below the melting-point of sodium nitrate, and only until the evolution of nitrous vapors has ceased. The residue is taken up in boiling water, the liquid decanted, and the alumina washed three or four times with water.[2]

The dish and the pestle are washed, and the wash-water, to which a few drops of nitric acid are added, is evaporated to dryness. The residue is taken up three times with boiling water in order to remove each time a fresh quantity of alumina which is mixed with the alkaline nitrate. Finally, it is treated with boiling water; after evaporation in a porcelain capsule, it is filtered, a slight excess of pure hydrochloric acid is added to the liquid and it is evaporated to dryness. A fresh quantity of hydrochloric acid is added and after evaporation, it is heated to 300° to drive out the excess of acid; the sodium chloride remaining is determined as silver chloride. From the weight of the latter the quantity of chlorine is calculated and the weight of sodium to which it corresponds.[3]

Estimation of the Carbon.—Two grams of the metal in form of shavings or filings are taken and ground in a mortar with 10 to 15 grams of powdered mercury bichloride, to which has been added a small quantity of water. The mixture is evaporated in a dish on a water-bath, then placed in a porcelain boat and heated in a current of pure hydrogen. This boat is introduced into a tube of Bohemian glass through which passes a current of oxygen free from carbon dioxide, and heated to redness. The gas is passed through a Liebig bulb containing a potash solution and two small U-tubes containing pieces of fused potash. The in-

[1] In this treatment, it is well to place a small funnel on the opening of the conical vessel, to retain the spray carried away by the evolution of the gas and the vapors.

[2] The first filtrate often deposits, on cooling, a variable quantity of alumina which assumes a gelatinous form.

[3] It is necessary during the above operations to protect the analysis from the glass powder which is so often found in the laboratory air.

crease in weight of the different tubes gives, as carbon dioxide, the quantity of carbon contained in the aluminum.

2. Analysis of Alloys of Copper and Aluminum.—*Estimation of the Copper.*—When the alloy contains as much as 6 per cent. of copper, 0.5 gram of the metal is dissolved in nitric acid free from chlorine, diluted to 50 cc., and the estimation is made by the electrolytic method of Lecoq Boisbaudran as given by Riche. The strength of current used is 0.1 ampere and the analysis is made in six hours if the temperature is kept at 60° and in twenty-four if it is made in the cold. When the electrolysis is complete, the copper, after having been washed and dried, is weighed in the metallic state.

Estimation of Silicon, Aluminum and Iron.—The copper being removed as sulphide by hydrogen sulphide, the alumina, iron and silicon are determined as has been previously shown.

Conclusions.—As an example we give a specimen of aluminum from Pittsburg:

Aluminum	98.82
Iron	0.27
Silicon	0.15
Copper	0.35
Sodium	0.10
Carbon	0.41
Nitrogen	trace
Titanium	"
Sulphur	none
	100.10

In the last few years the aluminum industry has made great progress from the standpoint of purity of the metal. The preceding analysis is a very good example, since it shows only 0.27 per cent. of iron and 0.15 per cent. of silicon. Three years before, a canteen made at Karlsruhe from an aluminum of Neuhausen gave the following figures:

Aluminum	96.12
Iron	1.08
Silicon	1.94
Carbon	0.30
	99.44

The comparison of these two analyses show that industry can

actually furnish a much purer metal. If aluminum, obtained by electrolysis, can be prepared free from sodium and carbon, we think that the preservation will be much easier.

We must remark, in conclusion, that the analytical results alone are not sufficient to give the value of the metal; it is necessary to add the mechanical properties, such as elongation, elastic limit and breaking strength.

CHAPTER IV

Carbides, Silicides, Borides, Phosphides, Arsenides, and Sulphides

METALLIC CARBIDES

The study of the metallic carbides has hitherto advanced very slowly. For a long time it has been known that certain metals on fusion dissolve varying quantities of carbon, but the carbides before my work included few others than the compounds formed by solution of carbon in a large excess of the metal.

The direct preparation of crystalline carbides is not possible in our laboratory furnaces, since the heat that these apparatus furnish is insufficient.

The electric furnace in which temperatures neighboring 3500° and beyond can be obtained has permitted the extension of the study under better conditions.

The results given by these researches are noteworthy on account of the applications which can be reaped industrially from the standpoint of the classification of the various simple bodies. The carbides were, in reality, formally regarded as poorly defined compounds, possessing new properties when determined, and forming a powerful support to the classification of the elements into natural groups in which the chemists of to-day have faith.

The property of decomposing water in the cold and giving pure acetylene is peculiar to the related metals, calcium, barium, and strontium. The carbides of aluminum and glucinum give pure methane. These are the characteristic reactions.

We have remarked in the beginning of our work on the electric furnace that if the electrodes are in contact with the fused lime there is formed a dark-colored compound having a crystalline fracture which is a combination of carbon and calcium. This body with water rapidly evolves a gas which has a peculiar odor, recalling that of acetylene.

Since our first publications on the preparation of artificial diamond and on the preparation of some refractory metals, we have undertaken the following studies, and the results obtained have been published first in the *Comptes rendus de l'Académie des Sciences*. We bring them together in this chapter.

Hitherto we have prepared only simple carbides, but there probably exist double carbides whose study merits further investigation.

A. Potassium Carbide

We have prepared in the electric furnace a large number of definite crystalline carbides, by reducing the metallic oxides or carbonates, with carbon. Some, such as the alkaline carbides, cannot be obtained in this manner. It seemed interesting to determine why these methods of preparation could not be applied to this series of compounds.

Berthelot[1] prepared potassium carbide by the action of acetylene on the alkaline metal at dull redness.

When a mixture of potassium carbonate and carbon ($K_2CO_3 + 2C$) is heated in the electric furnace with a current of 900 amperes at 45 volts, a black, pulverulent substance is obtained, composed of impure carbon, containing only traces of alkali metal, and not evolving gas in contact with water. Thus potassium carbide is not formed with a strong current.

In a second experiment we heated, in the electric furnace, in a carbon tube closed at one end, the mixture of black flux and carbon, which is used for the preparation of potassium. The heating lasted for eight minutes with a current of 45 volts pressure and 350 amperes. After cooling, the product taken from the tube was a coarse powder. Some portions had a fused homogeneous appearance, and the mass thrown into water evolved gas. If this black material was simply moistened with water it took fire, giving a gas which burned with a violet-red flame. Some particles gave slight explosion. Treated with water, in a tube containing mercury, it gave a slight evolution of gas. The black residue was formed of carbon, and the filtered solution showed a yellow color. This solution was strongly alkaline and contained a small quantity of carbonate and cyanide. The gas evolved contained a little nitrogen, hydrogen and acetylene. Two analyses of this gaseous mixture gave 70 per cent. and 66.6 per cent. acetylene. The evolution of gas was small, and the quantity of potassium carbide formed under these conditions was very small. These

[1] Berthelot: "Sur une nouvelle classe de radicaux métalliques composés," *Ann. chim. phys.*, 9, 384 (1886).

experiments demonstrate that the temperature of the electric furnace is much too high for the preparation of potassium carbide.

We observed that metallic potassium is slowly attacked in the cold and at the ordinary pressure by acetylene gas. If the experiment is somewhat prolonged, it can be made complete. In one experiment we placed a piece of potassium in the upper portion of a tube 0.5 meter long, closed at its upper end. This tube was filled with acetylene gas and placed on a mercury bath. The second day it was observed that the level of the mercury was raised. The absorption was slow, so we set the experiment away for forty-nine days. At the beginning the apparatus contained 17.3 cm. acetylene gas at 0° and 760 mm. After the experiment, the volume remaining was 8.335 cm., containing 4.348 cm. hydrogen (at 0° and 760 mm.). The volume of acetylene absorbed was 8.365 cm., which is double that of the hydrogen required by the following equation:

$$\frac{C_2H_2}{20} + K = C_2HK + \frac{H}{12}.$$

There is formed in the cold a white product[1] adhering slightly to the tube which is decomposed in contact with cold water, giving pure acetylene. The volume of gas collected was 7.3 cm., which was a little less than the theoretical quantity. The slight difference is due to the polymerization of a small quantity of acetylene. By the action of potassium on acetylene in the cold, the compound C_2HK (potassium acetylide) is formed as already shown by Berthelot, an intermediate product between acetylene, C_2H_2, and potassium carbide, K_2C_2.

B. Sodium Carbide

The reduction of sodium carbonate under the action of a strong current (1000 amperes at 70 volts) does not give the carbide. On the contrary, on heating, in a closed crucible placed in a carbon tube, a mixture of soda and sugar carbon with a weaker current of 350 amperes at 45 volts, a black powder is obtained

1 The transparent compound which was produced, possessed a blue color in the portion which was in contact with the metal. This color disappeared as the potassium was transformed. This phenomenon is similar to that assumed by potassium chloride at redness, in presence of the vapor of potassium, a coloration mentioned by Le Roux, *Compt. rend.*, 67, 1022 (1869), and which appears to result from a diffusion of the metal.

which, on contact with cold water, gives a slight evolution of acetylene.

The absorption of acetylene gas by sodium is much slower than by potassium, in fact, it takes place with greatest difficulty.[1]

On account of this feeble absorption we modified the experiment in the following manner: A sealed tube containing sodium and dry liquid acetylene was allowed to remain at the temperature of the laboratory. At the beginning, the action was somewhat slow, but after a time the sodium was tarnished and became covered with a yellowish white layer, whose thickness continually increased. Finally, the transformation of the metal was complete. The tube, strongly cooled, was subsequently opened and the gas collected over mercury. The excess of acetylene was readily separated from the free hydrogen. The yellow-white product which replaced the sodium was analyzed in the following manner: A definite weight of the substance was decomposed by water, and the acetylene collected and measured, and its purity was shown by analysis. The sodium was determined by an alkalimetric titration of the soda formed. The derivative thus obtained in the cold corresponds to the formula C_2HNa. An intermediate compound between acetylene and the carbide, sodium acetylide, is the product first formed.

It is not necessary in this preparation to use liquid acetylene; the same reaction takes place with compressed acetylene gas. The speed of the reaction appears to be a function of the pressure.

As we have remarked, the combination of sodium and acetylene takes place only with difficulty at the ordinary pressure, and requires many months to become perceptible. Under a pressure of one atmosphere the combination is more rapid, and if it is gently heated under reduced pressure, the action is more rapid. At about 50° it is distinct, and we have been able to completely transform a small piece of sodium into the compound C_2HNa by keeping it for fifteen hours in contact with acetylene at 70°.

Dissociation of the Compound C_2HNa.—The white substance, C_2HNa, obtained by the action of acetylene in the cold on sodium

[1] The more ready formation of potassium acetylide explains why Berthelot found traces of acetylene in hydrogen produced by the decomposition of water with potassium, while he found none in the hydrogen obtained by means of sodium.

was introduced into a Bohemian glass tube closed at one end; the other end of the tube rested on a mercury bath. When the compound is slowly heated in vacuum, it darkens, and pure acetylene gas is evolved. On further heating, the coloration becomes darker, acetylene is evolved, and on the cold part of the tube, a small quantity of solid and liquid hydrocarbons condenses. By stopping the experiment before the tube melts, the solid product, which remains as a residue, evolves pure acetylene gas with cold water. It is the sodium carbide of Berthelot, having the formula C_2Na_2. If instead of decomposing the product by water it is heated nearly to redness in vacuum, the substance no longer evolves gases. Black carbon remains on the bottom of the tube[1] and a bright ring of metallic sodium is seen condensed above the heated part.

By elevating the temperature to just below the softening point of Bohemian glass, sodium carbide in vacuum is decomposed into carbon and sodium. This explains the failure of our experiments on the reduction of soda or sodium carbonate with carbon. The temperature of the electric furnace was much too high for sodium carbide to exist. The preceding experiments can be represented by the equations:

$$2C_2NaH = C_2H_2 + C_2Na_2$$
$$C_2Na_2 = 2C + 2Na.$$

C. Lithium Carbide

Preparation.—To prepare lithium carbide, a mixture of carbon and lithium carbonate in the following proportion is heated in the electric furnace:

$$Li_2CO_3 + 4C = Li_2C_2 + 3CO.$$

This preparation is made in a carbon tube closed at one end. At the beginning of the experiment only a very little metallic vapor is evolved; as the experiment proceeds the reaction becomes violent and finally complete.

If the preparation is stopped at the time when an abundant evolution of metallic vapors commences, there is found on the bottom of the tube a white substance which has a crystalline fracture and which is lithium carbide. If, on the contrary, the heating

[1] After the experiment, we observed that this powder was formed of pure carbon. It gave no gas in contact with water.

is continued until the reaction has ceased, there is found in the upper part of the tube fused drops of carbide and the strongly heated part contains only graphite. Lithium carbide is volatile or is decomposed into its elements at a high temperature. The length of the experiment is consequently of great importance from the standpoint of yield of the carbide.

Lithium carbide is more easily decomposed by heat than calcium carbide. The temperature of decomposition of lithium carbide is between that of sodium carbide and the alkaline earths. With a current of 350 amperes at 50 volts the mixture should be heated ten to twelve minutes. On the contrary, with a current of 950 amperes at 50 volts the metallic vapors appear in abundance in four minutes, and the operation should be stopped immediately in order to obtain fused carbide in the hotter portion of the tube. Lithium carbide can also be obtained mixed with a small quantity of carbon by heating lithium in a current of acetylene at the temperature of a good coke fire.

Properties.—Lithium carbide appears as a crystalline mass, as transparent as an alkaline fluoride or chloride; on examining it with a microscope, bright crystals are found, which are very readily altered by the action of the moisture of the air. Its density is 1.65 at 18°; it is somewhat brittle and does not scratch glass.

It is a very energetic reducing agent; it is also richer in carbon than any carbide that we have prepared, in that it contains 69 per cent. of carbon. It takes fire in the cold in fluorine and in chlorine, and burns brightly, giving the fluoride or the chloride of lithium. In order to take fire in the vapor of bromine or in the vapor of iodine it must be slightly heated. Below redness it takes fire and burns brightly in oxygen, in the vapor of sulphur and selenium. It burns energetically in the vapor of phosphorus, giving a phosphide which is decomposed by cold water with evolution of hydrogen phosphide. Arsenic combines only at redness.

Potassium chlorate and nitrate at the melting-point oxidize this compound with evolution of light.

Fused potash attacks it with great evolution of heat. The concentrated acids act slowly. Lithium carbide is decomposed by

water in the cold, giving pure acetylene gas. This reaction, rapid at the ordinary temperature, becomes violent at 100°. In all points it is similar to the crystalline carbides of calcium, barium and strontium. A kilogram of lithium carbide gives, on decomposition with water, 587 liters of acetylene gas.

Analysis.—The analysis of lithium carbide was made by decomposing a weighed quantity of the substance with water in a graduated tube on a bath of mercury. The volume of acetylene obtained was measured, and account taken of the gas dissolved in the water which was used in the reaction. By a simple alkalimetric titration made on the latter liquid, the weight of the lithium oxide and the corresponding weight of lithium was obtained.

We obtained the following figures:

	1.	2.	3.	Theoretical for Li_2C_2.
Carbon	62.85	62.92	62.97	63.15
Lithium	36.31	36.29	36.40	36.84

CARBIDES OF THE ALKALINE EARTHS

Historical.—In 1862 Berthelot,[1] in a classical work, showed the properties of acetylene gas evolved from copper acetylide by hydrochloric acid. At the end of the same year Wöhler[2] showed that by the action of carbon on an alloy of zinc and calcium a black, pulverulent mass is obtained which contains an excess of carbon, and which in contact with cold water evolves a mixture of different gases. Among the latter he recognized acetylene qualitatively. The complete analysis of the mixed gases was not made.

We also recall that in another series of experiments, Winkler[3] has shown the reduction at redness of the carbonates of the alkaline earths by magnesium.

Maquenne,[4] in 1892, repeated and studied more completely this reaction; he prepared an impure amorphous powder of barium carbide, which in contact with water gave acetylene that contained

[1] Berthelot: "Recherches sur l'acétylène," *Ann. chim. phys.*, 3e série **67**, 52 (1863).

[2] Wöhler: "Preparation of Acetylene from Calcium Carbide," *Ann. Chem. Pharm.*, **124**, 220.

[3] Winkler: *Ber. d. chem. Ges.*, **23**, 120, and **24**, 1966.

[4] Maquenne: "Sur une nouvelle preparation de l'acétylène," *Ann. chim. phys.*, 6e série, **28**, 257.

only 3 to 7 per cent. hydrogen. This black powder gave about 50 liters of gas per kilogram. It was impossible for Maquenne, as he stated, to prepare calcium carbide by this method.[1]

The following year Travers, in London (February 6, 1893), by heating, in a Perrot furnace, a mixture of calcium chloride, powdered carbon and sodium, obtained a gray mass containing about 16 per cent. of calcium carbide which was decomposed by water.[2] He used this formation of acetylene gas in the preparation of mercury acetylide.[3]

The question arises at this point whether in a paper sent to the *Comptes rendus de l'Académie des Sciences,* December 12, 1892, I first published the preparation, in the electric furnace, of calcium carbide fusible at a high temperature. What I wrote on this subject is "If the temperature attains 3000°, the material of the furnace, the quicklime, fuses and becomes as fluid as water. At this temperature carbon rapidly reduces calcium oxide and the metal is produced; it readily unites with the carbon of the electrodes to form calcium carbide, which is liquid at redness and easy to collect."

Following this work I presented to the Académie des Sciences, a new paper on calcium carbide, March 5, 1894, and another on the carbides of barium and strontium March 19, 1894. In this work, I showed that at the high temperature of the electric furnace there can exist only one compound of carbon and calcium, which is crystalline; I established the formula by analysis, and studied its properties. I showed that this substance decomposed cold water, forming absolutely pure acetylene gas—the beginning of the acetylene industry. In this connection I ought to give a word of credit for the industrial research to Wilson, an American engineer.

At the end of the United States patent No. 492,377 on the preparation of aluminum bronze, which was taken out February

[1] I would say that barium carbonate is the only compound of the alkaline earths which can be transformed into carbide by the action of magnesium; the others, particularly calcium carbonate, are only incompletely acted on and give, when treated with water, a mixture of hydrogen and impure acetylene (Maquenne).

[2] Morris W. Travers: "A Method for the Preparation of Acetylene," Proceedings of the Chemical Society," February 6, 1893.

[3] R. T. Plimpton and W. Travers: "Metallic Derivatives of Acetylene: Mercuric Acetylide," *J. Chem. Soc.*, **65**, 264 (1894).

12, 1893, Thomas Wilson made a short allusion to an undetermined calcium carbide, as well as to a large number of other elements or compounds.

But this quotation is without scientific value, since Wilson gave no analyses of the products obtained and likewise did not observe that the product decomposes cold water with evolution of a gas. Moreover, the publication of the patent of Wilson was after our first notice on the electric furnace, in which we showed the formation of pure calcium carbide[1] along the electrodes.

Wilson, who carefully avoided all fused baths, probably looked for metallic calcium; if he had not the luck to discover crystalline calcium carbide, it is to him, in large part, that this compound owes its notoriety in North America.

D. Preparation of Calcium Carbide

An intimate mixture is made of 120 grams of lime from marble with 70 grams of sugar carbon; part of this mixture is placed in a crucible in the electric furnace and heated for fifteen minutes with a current of 350 amperes at 70 volts. Under these conditions there is formed a carbide or acetylide having the formula CaC_2, according to the following equation:

$$CaO + 3C = CaC_2 + CO$$

The lime is added in excess, since the crucible gives the quantity of carbon necessary for the formation of a definite carbide. The yield is about 120 to 150 grams. Calcium carbonate can be substituted for lime in this mixture, but this proceeding is not so good on account of the large volume of the substances used. In this case the following equation shows the proportion of calcium carbonate and carbon:

$$CaCO_3 + 4C = CaC_2 + 3CO.$$

The product, obtained in the two experiments, has the same appearance. It is a black homogeneous mass which has been fused and takes the form of the crucible.

In this preparation it is necessary that the lime and carbon be intimately mixed. An excess of powdered carbon should be avoided, as fused lime can not readily act on it and only a very little carbide is formed. If a liquid bath is not obtained,

[1] Moissan: *Compt. rend.*, de l'Académie des Sciences de Paris, December 12, 1892.

the preparation is poor and the resulting powder gives only a feeble evolution of gas with water and sometimes none. By using higher currents (1000 amperes at 60 volts) we repeated the experiment on a kilogram of the mixture of lime and carbon.

If an excess of lime is employed, metallic calcium appears as the following experiment demonstrates: In the cavity of a quicklime electric furnace a mixture of lime and carbon in the proportions indicated in the following equation was introduced:

$$CaO + C = Ca + CO$$

The furnace had in the center of its side a circular opening 2 cm. in diameter in which was placed an iron tube, covered on the outside with a lead spiral through which a current of cold water passed.

After the furnace had been heated for seven or eight minutes with a current of 350 amperes at 50 volts, an abundant evolution of vapors appeared, while very bright white flames as long as the electrodes issued from the furnace. The vapors which passed through the cold iron tube left a gray deposit, which, in contact with water, gave a large quantity of hydrogen containing traces of acetylene.

As we have previously remarked, it was impossible to unite the very finely divided calcium and form an ingot.

In our first experiments we used lime from pure marble. If the lime contains sulphates, phosphates or silica, the results are a little different. Some of these impurities can be found in the acetylene gas. Sulphur is found as organic sulphides.

To determine the influence of these compounds, we heated, by means of the arc, a mixture of sugar carbon and calcium sulphate. The mixture corresponded to the equation $CaSO_4 + 4C$. After completely drying in the Perrot furnace, it was placed in the electric furnace in a carbon tube, closed at one end. Length of heating, five minutes (900 amperes at 60 volts). The product collected at the bottom of the tube was well fused; it showed a crystalline fracture, but was only slowly decomposed by water, giving a small yield of gas. The gas contained 99.2 per cent. of acetylene. This mixture, treated with dilute hydrochloric acid, gave a rapid evolution of gas, which, after absorption by potash,

then treated with ammoniacal cuprous chloride, gave the following results:

	1.	2.
Hydrogen sulphide.....	56.20	57.00
Acetylene.....	43.30	42.60

The same experiment repeated with barium sulphate and carbon, in the same proportions, gave a well-fused crystalline mass, which evolved only a little acetylene with water. On the contrary, with dilute hydrochloric acid, energetic action took place and a gaseous mixture was set free, which on analysis contained:

	1.	2.
Hydrogen sulphide.....	88.20	86.90
Acetylene.....	11.40	12.80

Barium phosphate, mixed with a quantity of sugar carbon, sufficient for complete reduction, was heated for three minutes in a carbon tube with a current of 950 amperes at 70 volts. A well-fused mass, crystalline and having a dark brown color, was found.

This substance was decomposed by cold water and gave a copious evolution of a gas having a garlic odor. In order to separate the hydrogen phosphide which it contained, it was treated with a solution of copper sulphate. The acetylene was estimated in the gas by means of ammoniacal cuprous chloride. We obtained the following results:

	1.	2.
Acetylene.....	89.00	88.50
Hydrogen phosphide (PH_3)	10.90	11.30

The same experiment was repeated with the three sulphates and phosphates of the alkaline earths; the results were similar, although the volume of gas evolved with water varied. But if these mixtures are heated for a long time in the electric furnace or by a more powerful arc, it is possible to volatilize all of the sulphur or phosphorus and obtain an alkaline earth carbide, the only compound which is stable at a very high temperature.[1] These experiments show that in the technical preparation of calcium carbide, lime, which contains phosphate, should not be used. The latter is easily reduced by carbon and gives a phosphide decomposed by water with formation of hydrogen phosphide.

[1] We made some similar experiments on the arsenates of calcium and barium and with increasing temperatures obtained first a mixture of the carbide and arsenide, and finally a carbide free from arsenic.

We would add that lime mixed with magnesia only gives calcium carbide with difficulty. This seems to be explained by the fact that magnesia forms no carbide in the electric furnace, and consequently acts as an inert substance which retards the fusion of the mass.

Physical Properties.—Calcium carbide cleaves easily, and shows a distinctly crystalline fracture. The crystals, when detached, have a golden color, are opaque and bright. The thin leaves, examined under the microscope, are transparent and have a dark red color. These crystals do not appear to be isometric. Their density at 18° in benzene is 2.22; this carbide is insoluble in such solvents as carbon disulphide, petroleum and benzene.

Chemical Properties.—Hydrogen does not act on calcium carbide either in the warm or cold. This compound, at the ordinary temperature, takes fire in fluorine gas with the formation of calcium fluoride and carbon fluoride.

Dry chlorine is without action in the cold. At 245° the carbide takes fire in chlorine; calcium chloride is formed with the separation of carbon, but the weight of this element is less than the weight of the carbon in the carbide.

Bromine acts at 350° and the vapor of iodine decomposes the carbide with evolution of light at 305°.

Calcium carbide burns in oxygen at dull redness, giving calcium carbonate. In the vapor of sulphur it takes fire at about 500° with formation of calcium sulphide and carbon disulphide.

Pure dry nitrogen does not act on it at 1200°. The vapor of phosphorus at redness transforms calcium carbide into phosphide without causing it to take fire. The vapor of arsenic, on the contrary, acts with great evolution of heat, forming calcium arsenide.

At a white heat, silicon and boron are without action on the compound. Fused calcium carbide dissolves carbon which separates in the form of graphite. Calcium carbide does not react with most of the metals. It is not decomposed by sodium and magnesium at the temperature of the softening of glass. With iron there is no action at dull redness, but at a high temperature, an alloy of iron and calcium carbide is formed.

Tin is without action at redness, while antimony, at the same

temperature, gives a crystalline alloy containing calcium. The most curious action presented by this carbide is with water. If an inverted tube is filled with mercury and a piece of the carbide introduced, then a few cubic centimeters of water are added, a violent evolution of gas is immediately produced which does not cease until all the carbide is decomposed; calcium hydroxide remains suspended in the liquid. The gas is pure acetylene completely absorbed by ammoniacal cuprous chloride and leaves in the upper part of the tube only an almost imperceptible quantity of impurity. This decomposition of water is produced with evolution of heat, but without evolution of light. It is as energetic as that produced by sodium in contact with water.

From the weight of the carbide taken and from the volume of the gas, the reaction is represented by the following equation:

$$CaC_2 + H_2O = C_2H_2 + CaO$$

This decomposition appeared in our work as soon as the carbide came in contact with a liquid containing water. This calcium carbide or acetylide affords then a ready means of obtaining pure acetylene as has been shown by Berthelot in his study on this compound. The gas obtained is pure acetylene, since eudiometric analyses have given the following figures:

Gas analyzed	1.28
Oxygen	15.15
Total gas	16.43
After sparking	14.50
After the action of caustic potash	11.98
Contraction	1.93
Carbon dioxide by difference	2.52

If the gas was acetylene, C_2H_2, we would theoretically have 1.95 as contraction and 2.56 as the volume of carbon dioxide.

Another eudiometric analysis gave identical results. This proof was quite sufficient to establish the purity of the gas obtained. We, however, determined the density of the hydrocarbon.

Two experiments gave the figures 0.907 and 0.912. Berthelot has shown that the density of acetylene is 0.92 and the theoretical density is 0.90. If the water vapor is allowed to act at a red heat on calcium carbide, the reaction proceeds with much less energy. The carbide becomes covered with a layer of carbon and

carbonate which prevents the action of the water vapor, and the evolution, consisting in large part of hydrogen and acetylene, is much less rapid. Acids act on the carbide, especially when dilute. With fuming sulphuric acid, gas is slowly evolved and appears to be largely absorbed. The ordinary acid gives a more energetic decomposition, and a marked odor of aldehyde is observed.

Fuming nitric acid has no action in the cold, and scarcely any on boiling. Dilute nitric acid gives acetylene. A dilute solution of hydriodic acid also evolves pure acetylene. This is true with a solution of hydrochloric acid. On the contrary, heated in hydrochloric acid gas to red heat it takes fire and evolves a gaseous mixture rich in hydrogen.

Oxidizing agents act with great energy on the compound. Fused chromic acid takes fire in contact with calcium carbide, evolving carbon dioxide. The aqueous solution of chromic acid only sets free acetylene from the carbide. Fused potassium chlorate and nitrate apparently do not attack calcium carbide. It must be heated to redness, when it decomposes with evolution of light and formation of calcium carbonate. Lead dioxide oxidizes it with evolution of light below redness and the lead formed in the reduction contains calcium. Calcium carbide, ground with lead fluoride, at the ordinary temperature, glows. Heated at 180° in a sealed tube with absolute alcohol, calcium carbide gives acetylene and calcium ethylate,

$$2C_2H_5OH + CaC_2 = C_2H_2 + CaC_2H_5O.$$

The acetylene gas obtained by this reaction can be completely absorbed by ammoniacal cuprous chloride, but it gives a black carbide which seems to indicate the existence of hydrocarbons of the acetylene series.

The violent action of acetylene on chlorine, shown by Berthelot,[1] can be demonstrated in the following manner: In a flask containing cold water saturated with chlorine, some pieces of calcium carbide are introduced. Some bubbles of acetylene are immediately evolved which take fire in contact with the chlorine; at the same time the odor of the chlorides of carbon can be readily detected. This form of decomposition gives a beautiful lecture experiment.

[1] Berthelot: "Recherches sur l'acétylène," *Ann. chim. phys.*, 3e série, **67**, 52.

Analysis.—The content of calcium was determined after decomposition of the carbide by water, taking into account Nos. 3 and 4, which left, after the action of the water, a small quantity of insoluble graphite. The carbon was estimated by difference, by loss of the weight of acetylene gas in a small apparatus similar to that which is used in the analysis of carbonates. The carbon was estimated by collecting over mercury the gas evolved from a given weight of carbide placed in a graduated tube and subsequently adding a small quantity of water. The two methods gave the following results:

1. 0.1895 gram of carbide evolved 64 cc. of gas with 4 cc. of water. The liquid theoretically dissolving its volume of acetylene, there was produced 68 cc. of gas. Theoretically at 15° and 760 mm., 0.1895 gram of the carbide, CaC_2, should give 68 cc.

2. 0.285 gram of carbide gave 96.5 cc. with 4 cc. of water, or a total of $96.5 + 4 = 100.5$. Theoretically, 102 cc. should be obtained.

The determinations of carbon and calcium in the crystalline compound that we described, gave the following figures:

	1.	2.	3.	4.	Theoretical.
Calcium	62.7	62.1	61.7	6.20	62.5
Carbon	37.3	37.8	...	...	37.5

Consequently, as soon as the temperature is sufficiently high, metallic calcium or its compounds, in contact with carbon, forms a carbide or acetylide having the formula CaC_2. This reaction can possibly be of some interest in geology.

It is probable that, in the first geological periods, the carbon of the vegetable or mineral kingdoms existed in the form of carbides. The large quantity of calcium on the surface of the earth, its distribution in all of the formations, early or recent, permits the view that it has played a part in this fixation of carbon under the form of a metallic compound.

Moreover, Berthelot[1] has already shown that the action of water vapor on the acetylides of the alkalies or alkaline earths can explain the formation of carbides and the different carbonaceous materials.

[1] Berthelot: "Sur l'origine des carbures et des combustibles minéraux," *Ann. chim. phys.*, 4e série, 9, 481.

We add that the action of the air on calcium carbide, giving carbon dioxide at redness, permits the explanation of the passage of carbon from a solid carbide to the gaseous form of carbon dioxide. This latter then can be assimilated by the vegetable kingdom.

Decomposition of Calcium Carbide by Heat.—Some of the experiments made in the electric furnace have shown that calcium carbide can be decomposed by a current of great intensity:

(1) When we heated small quantities of calcium carbide with currents of 1200 amperes at 60 volts, if the experiment lasted ten minutes, a residue of pulverulent graphite was obtained which only contained traces of calcium carbide.

This did not come from the volatilization of the compound since carbon powder remained in the crucible. It was more likely due to a dissociation of the carbide, calcium distilling and pulverulent carbon remaining as residue.

(2) In the experiments made by means of the cold tube of Deville, which was used to study the condensation of the vapor of carbon, we never obtained condensations of calcium carbide. If fused calcium carbide is heated in the electric furnace, only a powder of graphite, lime and calcium is found on the copper tube, through which cold water passes. The powder in contact with water evolved hydrogen whose purity was determined by eudiometric analysis. Like the carbides of sodium and lithium, but at a much higher temperature, calcium carbide can be decomposed into the metal and carbon.

Color of Calcium Carbide.—We have seen that the crystals of calcium carbide had a reddish brown, opaque and bright appearance, and the substance in thin leaves under the microscope appeared dark red. Recent investigations have shown that the coloration and appearance is due to impurities. Calcium carbide containing no iron at all is as transparent as sodium chloride.

We give, as an example, the following experiments:

(1) When metallic calcium is heated to dull redness[1] in a layer

[1] This synthesis of calcium carbide is made at a low temperature; it can be effected by heating the mixture of carbon and calcium in a porcelain crucible with the flame of an alcohol lamp. The heat evolved by the union of carbon and calcium is sufficiently high to cause the fusion of the calcium carbide, a fusion which heretofore has been attained only in the electric furnace.

of pure amorphous carbon, prepared by the sudden decomposition of acetylene, white calcium carbide is obtained, which decomposes cold water with the formation of calcium hydroxide and evolution of acetylene. This carbide, examined under the microscope, is formed of a mass of transparent crystals.

(2) When calcium hydride, CaH_2, prepared by the direct union of calcium with hydrogen, is heated in a layer of pure amorphous carbon, white calcium carbide, CaC_2, is obtained in thin leaves which are completely transparent.

(3) A similar result is obtained when the preceding experiment is repeated with crystalline calcium nitride, CaN_2.

(4) Ammoniacal double acetylide of calcium, $CaC_2,C_2H_2,4NH_3$, that we obtained at — 60° by the action of acetylene on calcium ammonia, gives, on decomposition, a pure white calcium carbide which under the microscope is transparent. We mixed this white calcium carbide with a small quantity of iron oxide and fused it in the electric furnace in a crucible of pure graphite. On cooling, a red-brown calcium carbide was obtained similar in appearance to that prepared commercially.

Pure calcium carbide is transparent; when it is chestnut-colored or red-brown, the color is due to the presence of iron, a trace of this metal being sufficient to produce this coloration.

Analysis of Some Specimens of Commercial Calcium Carbide.— Since our first publications on the formation of crystalline calcium carbide by means of the electric furnace, this preparation has become of technical importance and to-day it is prepared in large quantities.

Although the question at first sight seems simple, the preparation of tons of carbide present some difficulties. The careful preparation of the mixtures, the nature of the lime and the carbon, and the conduct of very large electrodes, which carry intense currents, have been as difficult as the questions which have been successively studied and which have to-day been in large part solved. The introduction and application of the bright burning gas which is produced from this preparation still presents some difficulties, but these problems, since later investigations, seem to be in a fair way toward solution.

At the beginning of this industry, the choice of the substances which entered into the reactions, calcium oxide and carbon, left much to be desired. The first manufacturers who undertook the preparation used as carbon, coke containing a large quantity of mineral matter rich in sulphur and phosphorus. The lime used was of any kind, nearly always containing the silicates, aluminum, phosphates and sulphates.

There is apparently no reason why such a mixture was used, since the electric furnace gave a very impure calcium carbide. The carbide contained sulphur, aluminum, calcium phosphate, the silicides, in fact, silicides decomposed by water. In contact with a small quantity of water it immediately gave very impure acetylene, contaminated with hydrogen phosphide and hydrogen sulphide.

In order to increase the profits or from ignorance, the manufacturers at first produced impure calcium carbide and from it very impure acetylene. This poor preparation was the cause of the first difficulties which were encountered in the application of acetylene to lighting. It is thus seen that it is necessary to start in with pure lime and carbon which is as free as possible from mineral matter.

To-day, the manufacture is made under the best conditions. There is found in trade fused, homogeneous calcium carbide having a crystalline fracture and a characteristic red-brown appearance. This carbide is always preferred for the manufacture of acetylene gas. In spite of the peculiar appearance of calcium carbide it is well to make an analysis of it. Many methods have been given and the one by Lunge and Cedercreutz[1] in which a definite weight of calcium carbide is precipitated by an excess of water and weighed, gives the best results. The great difficulty consists in obtaining a homogeneous sample when working with a quantity of any value.

Theoretically, 1 kilo of calcium carbide should give 349 liters of acetylene gas. On decomposing some samples of calcium carbide with milk of lime, previously saturated with acetylene gas, we obtained (at 0° and 760 mm.) the following volumes:

[1] Lunge and Cedercreutz: *Ztschr. angew. Chem.*, **651**, 1897.

	1.	2.	3.	4.	5.	6.	7.
V° ...	292.81	294.10	301.30	304.60	307.72	316.41	318.77

If, on the contrary, the calcium carbide has not a fused and crystalline appearance, if it is porous and grayish, its value is much less. Samples of this gave 228.60, 250.40 and 260.30. We have not studied the impurities of acetylene gas. They have been studied.[1] We would only remark that some specimens contained somewhat large quantities of ammonia. Chuard[2] observed this fact and found 0.03 and 0.06 per cent. ammonia in the gas, and from 0.24 to 0.40 per cent. nitrogen in the residue.

In four experiments made on four different specimens we obtained the following figures:

	1.	2.	3.	4.
Total nitrogen	0.02	0.12	0.15	0.31

Many of the carbides gave a small quantity of hydrogen phosphide; some gave none. The investigation of the insoluble residue left by calcium carbide on decomposition with water was investigated. To more readily study this residue we decomposed calcium carbide by an aqueous solution of sugar in order to keep the lime in solution as calcium sucrate. The somewhat small residue (we worked with 10 grams of carbide) was brought on a filter washed with a solution of sugar, then pure water, both of the liquids being free from carbon dioxide. It was then treated with alcohol and finally with ether, and dried at 40° *in vacuo*. Examined with the microscope, the residue contained carbon silicide, a silicide of calcium and iron, white particles rich in lime, sometimes a little calcium sulphide and graphite. If this residue is treated with 1 : 10 hydrochloric acid it partially dissolves, and in the solution, iron, lime, a small quantity of alumina, and phosphorus are found. The carbon silicide and the graphite always remain unattacked. The calcium sulphide dissolves. It was then treated with concentrated hydrochloric acid, when lime, iron and silica passed into solution. There is no relation between the quantities of the insoluble matter and the quality of the acetylene.

[1] C. Wilgerodt: *Ber. d. chem. Ges.*, **2107**, 1895; De Brevans: "L'Éclairage a' l'acétylène, 2e Congrés international de chimie appliqués," Vol. III, p. 506: Goiand: "Analyse de l'acétylène obtenu par le carbure de calcium," *Ibid.*, p. 574; Bergé and Reychler: *Bull. Soc. Chim.*, **17**, 218 (1897).

[2] Chuard: "Sur le produits de decomposition du carbure de calcium par l'lav." *Bull. Soc. Chim.*, **22**, 678 (1897).

The different treatments made on the same samples gave the following figures:

	1.	2.	3.	4.	5.
Treatment with sugar solution	3.40	5.3	3.2	3.9	3.4
Treatment with 1 : 10 hydrochloric acid .	2.10	1.9	1.5	2.4	1.4
Treatment with concentrated hydrochloric acid	1.70	1.7	1.4	2.2	1.1

After this treatment and by comparing the residues with the microscope, we were able to determine in what condition the most of the impurities existed.

Silicon.—The silicon is found mostly as carbon silicide. This compound is easily recognized under the microscope and by its hexagonal crystals which are colored green and blue and which are characteristic. It can be readily separated from the other substances by reason of its stability and the density of 3.121. If the residue from calcium carbide is treated alternately with boiling sulphuric acid and hydrofluoric acid, only carbon silicide and graphite remains. With bromoform, whose density is 2.9, these two substances can be separated.

Silicon is sometimes found as calcium silicide, as Le Chatelier has shown.[1] There is found, in this mixture, small spheres having a metallic fracture and containing iron, carbon and silicon. There is also found the piles of crystals of silica described by Marsden.[2] For our part, we never found that calcium carbide took fire in the air, under the action of a small quantity of water by the inflaming of hydrogen silicide. On the contrary, it frequently happened, in the treatment of the residues with concentrated hydrochloric acid, that hydrogen silicide was evolved. This gas arose from the decomposition of the calcium silicide.

Sulphur.—In the samples studied we found sulphur as calcium sulphide or aluminum sulphide. We detected the presence of calcium sulphide in some residues, which remained after the action of the sugar solution, by a microchemical reaction, using a dilute solution of lead acetate and a few drops of acetic acid. The white particles of calcium sulphide became black. Hydrogen sulphide

[1] Le Chatelier : "Sur les impuretes du carbure de calcium commercial," *Bull. Soc. Chim.*, Paris, **17**, 793 (1897).

[2] Marsden : Proceedings of the Royal Society, **20**, 1880–81, Edinburgh.

is not evolved by the action of water on the calcium sulphide, in presence of calcium hydroxide.

To demonstrate this we took a small quantity of pure crystalline calcium sulphide which was prepared in the electric furnace, reduced it to a powder and treated it with concentrated milk of lime. The filtered liquid gave no black precipitate with a lead salt. We observed, on the contrary, that all of the carbides which we studied gave, with an excess of water, milk of lime, whose clear solution with lead salts gave a black precipitate containing sulphur and traces of phosphorus. There appears to be complex reactions between the calcium hydroxide and the calcium sulphide. The milk of lime, *in vacuo*, did not lose hydrogen sulphide.

Nevertheless, hydrogen sulphide is not found in the acetylene gas evolved when the carbide is decomposed by water. The milk of lime which is formed always tends to retain the hydrogen sulphide.

In the preparation of calcium carbide, the sulphates, which the lime contains, are reduced with the formation of calcium sulphide which is not decomposed by water. If the lime contains aluminum silicates, the silicon, with the carbon, forms carbon silicide, and if sulphur exists as sulphate or sulphide, it can form aluminum sulphide which is decomposed by cold water with formation of hydrogen sulphide. Mourlot,[1] on heating aluminum and stibnite in the electric furnace, obtained fused aluminum sulphide having a crystalline fracture and perfectly stable at this high temperature. Calcium carbide, prepared under these conditions, can then contain aluminum sulphide and in contact with cold water evolve hydrogen sulphide.

Sulphur ought not to be found as silicon sulphide. We give, on this point, the following experiment: When impure aluminum containing silicon is heated in a boat in a current of hydrogen sulphide to redness, fused aluminum sulphide is formed in the boat, and in the cold part of the tube a ring of silicon sulphide is found. The latter compound is volatile and does not appear in the calcium carbide prepared in the electric furnace.

When calcium carbide contains calcium sulphide, it gives, by

[1] Mourlot : "Sur l'action d'une haute témperature sur quelques sulfures," *Compt. rend.*, **123**, 55 (1896).

decomposition with water, small quantities of a sulphur-containing organic compound which differs from hydrogen sulphide. This can be shown as follows: Acetylene gas, produced by the decomposition of carbide with water, was passed through two Liebig bulbs which contained copper nitrate or better, potash; or, still better, lead nitrate. It was then burned and the gases drawn through a small quantity of distilled water kept at 0°. In three cases it formed, by combustion, a small quantity of sulphuric acid which was subsequently detected. The Liebig bulbs retained all of the hydrogen sulphide and allowed a sulphur compound to pass through.[1] A blank experiment was made under the same conditions with the laboratory air, but nothing resulted. The best reaction was produced after washing the acetylene by an alkaline solution.

In this experiment the first Liebig bulb, containing the copper nitrate or the lead salt, blackened under the influence of the hydrogen phosphide, but after the experiment only contained traces of sulphur. Frequently it contained none and the gas was free from hydrogen sulphide. The estimation of the total sulphur made on three samples of calcium carbide gave 0.37 per cent., 0.43 per cent. and 0.74 per cent.[2]

Iron.—Iron is found as silicide and carbo-silicide. Its content is very variable and depends largely on the purity of the carbon used.[3]

Phosphorus.—This non-metal is the most troublesome impurity in calcium carbide. The most of it is found as calcium phosphide which is decomposed by water; some is also found in the small spheres which have a metallic appearance and contain iron and silicon.

[1] Lunge and Cedercreutz obtained the same results by washing the acetylene gas with a solution of lead acetate and then oxidizing by a solution of sodium hydrochlorite. They obtained a precipitate by barium chloride.

[2] This analysis was made in the following manner: Several grams of the carbide were decomposed with a small quantity of alkaline liquor, evaporated to dryness, and fused with a mixture of alkaline carbonate and nitrate. The fusion was dissolved in water, and, after filtering, the liquid was made acid with hydrochloric acid. After treatment with ammonia and filtration, the sulphur was determined. Pope has previously given a different method. Pope: "Estimation of Sulphides in Calcium Carbide," *J. Am. Chem. Soc.*, **18**, 740.

[3] In some carbides, rounded masses having a metallic appearance and containing iron are found, several centimeters through, which come from the fusion of the clamps which carry the electrodes. We have not studied these masses.

Carbon.—Some specimens of calcium carbide contained a quantity of graphite. The graphite we obtained was in very thin leaves, sometimes hexagonal, but more often distorted and irregular. This graphite did not swell, and energetically retained silica and calcium. Inasmuch as the diamond has been announced in technical calcium carbide, we made a special investigation of this variety of carbon. After treatment with water, then with concentrated hydrochloric acid, the residue obtained was submitted to the treatment that we described for the separation of the diamond from all kinds of impurities. Under these conditions we separated some round, transparent particles, which possessed no crystalline appearance and did not burn in oxygen. To make the combustion, we used the platinum boat that we described in the preparation of the artificial diamond. None of the specimens of calcium carbide that we studied contained the diamond.

Action of Calcium Carbide on the Oxides.—Fused calcium carbide reacts energetically on the oxides. If the metal does not unite with carbon as is the case with lead, tin and bismuth, it is liberated and can be separated or can be combined with other bodies according to the conditions of the experiment. If the metals or non-metals can unite with carbon, a double decomposition takes place according to the equation

$$RO + CaC_2 = CaO + RC_n$$

in which R represents any metal and n the number of carbon atoms which combines with it. We have thus been able to prepare compounds of aluminum, chromium, manganese, tungsten, titanium and silicon, already obtained by direct union or reduction of the oxide.

The two other alkaline earth metals, barium and strontium, readily form the crystalline carbides or acetylides whose properties are similar. We will briefly describe them.

E. Preparation of Barium Carbide

The carbon crucible of the electric furnace is filled with an intimate mixture of 50 grams of dry baryta with 30 grams of sugar carbon. On cooling, a black, fused mass is obtained, which assumes the form of the crucible and which is easily broken. On breaking, it shows large, leafy crystals. It is possible to substitute barium carbonate for

the oxide, when it is desirable to omit the preparation of the latter in pure condition. In this case, 25 grams of sugar carbon are added to 150 grams of pure barium carbonate, the whole is carefully mixed and heated as before. The yield is a little less than the latter preparation, but the product obtained is identical and corresponds to the formula BaC_2. We have previously seen, in connection with calcium carbide, that Maquenne, by the action of magnesium on barium carbonate, prepared impure barium carbide, which, with water, gave acetylene containing 3 to 7 per cent. of hydrogen.

F. Preparation of Strontium Carbide

Strontium carbide is obtained under the same conditions and with the same ease by heating, in the electric furnace, a mixture of 120 grams of strontia and 30 grams of sugar carbon or 150 grams of strontium carbonate and 50 grams of sugar carbon. Strontium carbide, SrC_2, also appears as a black mass with a red-brown fracture. Like the other alkaline earth carbides it decomposes in moist air.

Properties.—Barium carbide is the most fusible of the alkaline earth carbides; it has a density of 3.75. Strontium carbide has a density of 3.19. The carbides are attacked by fluorine with evolution of light and the formation of fused fluoride. They are immediately decomposed by water, like calcium carbide, giving the hydrated oxide and pure acetylene gas. The acids, either concentrated or dilute, have an action similar to that described with calcium carbide. The action of the halogens is energetic. In presence of the gaseous halogen, when the temperature is sufficiently high, the reaction takes place with evolution of light. In order to compare the different results, we give the temperatures taken with the electric pyrometer and by the thermometer, at the moment when they took fire.

	Temperature where light is evolved in		
	Dry chlorine.	Bromine vapor.	Iodine vapor.
CaC_2	245°	350°	305°
SrC_2	197°	174°	182°
BaC_2	140°	130°	122°

This action of the halogens is curious, while barium carbide readily combines with chlorine, bromine and iodine; it unites

with the latter element at a lower temperature than with bromine or chlorine. The reverse is the case with calcium carbide. The action of oxygen is also energetic, but at a much higher temperature. The temperature must reach the softening point of glass, and with barium carbide the experiment is very pretty. A bright glowing is produced at the same time fused baryta is formed. Barium carbide is decomposed with evolution of light by sulphur at a temperature slightly above the fusion-point of the latter substance. Barium sulphide and carbon bisulphide are formed. The same reaction takes place with strontium carbide at 500°.

Selenium acts similarly with bright light, forming carbon selenide and an alkaline earth selenide.

Nitrogen does not act at 1200°,[1] but the vapor of phosphorus acts energetically at dull redness, bright light is evolved, and the phosphide is formed.

With arsenic, the reaction is not so strong and requires a higher temperature. At 1000°, silicon and boron do not act on these alkaline earth carbides.

Analyses.—The determinations of carbon, barium and strontium were made by the methods given with calcium carbide.

The analyses gave the following results:

	1.	2.	Theoretical.
Strontium	77.96	78.32	78.47
Carbon	21.55	21.41	21.52
	1.	2.	Theoretical.
Barium	85.30	85.10	85.00
Carbon	15.10	14.87	15.00

These compounds correspond to the formula SrC_2 and BaC_2.

Conclusions.—The alkaline earth metals, calcium, strontium and barium readily unite with carbon at the temperature of the electric furnace, and give crystalline carbides. These bodies are decomposed by cold water with formation of the hydrated oxide and pure acetylene. This new method for the preparation of the carbides of the alkaline earths in the electric furnace has entered into practical industry since the publication of our first work. It affords the ready production of acetylene gas and the first application of this hydrocarbon to lighting seems to have given good

[1] The residue treated with boiling water after the evolution of acetylene, gave, however, some ammoniacal vapors.

results. The industrial preparation of calcium carbide has been studied in France particularly by Bullier, and in the United States by Wilson. This simple preparation of the alkaline earth carbides in the electric furnace can also produce some changes in the manufacture of baryta and strontia. These two oxides and their salts can be readily obtained by starting with the carbides formed by the action of carbon on the natural carbonates of barium and strontium. These carbides are decomposed by water, with formation of acetylene, giving hydrated strontia or baryta which could be transformed into chloride, chlorate or nitrate.

G. Cerium Carbide

Our work on the carbides of the alkaline earths led us to study the combinations of carbon with the cerite metals. We must mention that Otto Petterson, in a paper having the title "Contributions to the Chemistry of the Rare Earth Elements,"[1] prepared, by applying our electric-furnace method, the carbides of lanthanum, yttrium, erbium and holmium. Petterson has given no analyses of the hydrocarbons formed by the action of water. It is to this point that our experiments were particularly directed.

Preparation of Cerium Carbide.—Pure white cerium dioxide, CeO_2,[2] intimately mixed with sugar carbon in the following proportions:

Sugar carbon	48
Cerium oxide	192

These proportions correspond to the equation

$$CeO_2 + 4C = CeC_2 + 2CO.$$

The reduction is made in the electric furnace at a relatively low temperature. The oxide first fuses, then boils—due to the evolution of carbon dioxide. The heating is interrupted when the mass is in quiet fusion. This preparation was made in a carbon tube

[1] Petterson : Supplement to the Proceedings of the Swedish Royal Academy, Vol. II, p. 2, No. 1, 1895.

[2] In order to prepare the dioxide, cerite is first treated with sulphuric acid. The sulphates thus obtained are transformed into oxalates and the oxalates converted into nitrates. By applying to these nitrates the method of Debray, or better, by fusing the nitrates in a bath of sodium and potassium nitrates which melt at a low temperature, it is possible to precipitate the cerium as cerium oxide with the basic nitrates of lanthanum and didymium. On dissolving the nitrates in dilute sulphuric acid, pale yellow cerium oxide remains. This treatment is repeated three or four times in order to bring it into a sufficiently pure condition.

closed at one end. With a current of 300 amperes at 60 volts, the complete reduction of 100 grams of cerium oxide requires eight to ten minutes. When a current of 900 amperes at 50 volts is used, 600 grams of material are reduced in three minutes. We have had occasion in this work to prepare more than 4 kilos of cerium carbide.

Properties.—Cerium carbide appears as a homogeneous fusion having a crystalline fracture. It decomposes on exposure to the air, becoming covered with a yellow powder; at the same time there is evolved a characteristic garlic odor recalling that of allylene. Examined under the microscope, in benzene, the finely pulverized carbide shows crystalline fragments, among which are found transparent, hexagonal particles which have a yellow-red color. When it contains no graphite, the small, colored crystals are entirely transparent. The density of cerium carbide in benzene is 5.23.

Fluorine does not attack the carbide in the cold, but, by a slight elevation of the temperature, a bright evolution of light is produced, and a white volatile fluoride is formed.

Chlorine attacks it about 230°, forming cerium chloride which envelopes the graphite when the carbide contains it.

Bromine and iodine similarly evolve light, but at a higher temperature. In oxygen, cerium carbide burns brightly at redness, forming a crystalline residue of oxide and giving off carbon dioxide. The reaction is complete and by this means the metal and total carbon can be determined. The vapor of sulphur gives with evolution of light cerium sulphide which, in contact with acids, evolves hydrogen sulphide. Selenium acts below red heat.

Nitrogen and phosphorus are without action on cerium carbide at the temperature of the softening of glass.

Carbon dissolves in fused cerium carbide and crystallizes in the mass under the form of graphite.

Gaseous hydrochloric acid attacks cerium carbide at 650° with evolution of light. The chloride is formed, mixed with a voluminous carbonaceous residue; at the same time, hydrogen is evolved.

Hydriodic acid at dull redness gives an iodide under similar conditions. At redness, hydrogen sulphide gives a mixture of

graphite and cerium sulphide. At 600°, ammonia does not form nitride.

Oxidizing agents act energetically on this compound. Potassium chlorate attacks it with evolution of light as soon as it fuses. The decomposition is less energetic with potassium nitrate. Fused potash and potassium carbonate decompose cerium carbide with great evolution of heat, giving hydrogen and a yellow-white oxide. Concentrated sulphuric acid does not act in the cold, but in the heat, sulphurous acid is set free. Fuming nitric acid is without action, and dilute acid only acts on account of the water which it contains.

The most characteristic reaction of cerium carbide is that which it gives with water. On allowing some water to drop on a piece of the carbide, the temperature is raised so much that it vaporizes the liquid. With excess of water, the reaction, violent at the beginning, quiets down and is not complete until after ten or twelve hours. Cerium carbide forms, on decomposition, a white cerium hydroxide which, in contact with the air, takes on a wine coloration. The gas which is evolved is mainly acetylene and methane. On analysis, it gave the following results.[1]

	1.	2.	3.	4.	5.
Acetylene.....	75.00	75.50	76.69	76.42	75.64
Ethylene	3.52	4.23	....	....	....
Methane.....	21.48	20.27	....	....	....

These results were obtained with carbides free from calcium, and treated with an excess of water at the ordinary temperature.

This decomposition, giving a constant content of acetylene and methane, led to the thought that we had to deal with the two simple related bodies, the first of which gave acetylene, and the second methane; for example, that which would be formed by a mixture of alumina and lime changed into the form of carbides.

Consequently, we attempted to fractionate the cerium carbide by treatment with water, by very dilute mineral acids or by organic acids under different conditions, but our attempts were fruitless. The action of the high temperature of the electric furnace on cerium carbide, was tried in order to produce a partial distillation,

[1] To separate the different hydrocarbons, we followed the methods of Berthelot. The details are given under lanthanum carbide.

with the view of obtaining a purer carbide, but it gave no better results.[1] From these experiments we have drawn the following conclusions:

When cerium carbide is decomposed with ice-water, the proportion of the different hydrocarbons varies, as is shown by the following figures:

	1.	2.	3.
Acetylene	78.47	79.7	80.00
Ethylene.....	2.63	...	....
Methane	18.90	...	....

If cerium carbide is not decomposed by water but by dilute acids, the proportion of acetylene again varies. A cerium carbide which, with an excess of pure water at the ordinary temperature, gives a mixture of gases containing 71 per cent. acetylene and only 65.8 per cent. with dilute hydrochloric acid, with nitric acid gives 83 per cent.

Moreover, if the residue from the decomposition of cerium carbide by water is examined and if the liquid is extracted with ether, 3 to 4 per cent. of the combined carbon is found as hydrocarbons. The decomposition of cerium carbide by water is as complex as that of uranium carbide, which we shall describe later, but takes place without evolution of hydrogen. This complexity is due to secondary reactions which are produced according to the conditions and the temperature.

Analysis.—The cerium was estimated as CeO_2 by roasting the sulphate or nitrate or by direct combustion of the carbide in oxygen. The figures show little difference according to the method used; they are always a little higher than the theoretical, which appears probable from the fact that we used the atomic weight 141.

According to different chemists who have worked with cerium and according to Schützenberger, the oxide CeO_2 does not always have a constant composition. The total carbon was determined by direct combustion in oxygen and weighed as carbon dioxide.

The samples containing graphite were treated with nitric acid

[1] It should not be forgotten that in the long experiments made in the electric furnace, the cerium can take up a small quantity of calcium carbide. It should always be made sure that the cerium carbide thus treated contains no calcium.

and the content of graphite determined by weighing as carbon dioxide after combustion in oxygen.

The formula CeC_2 requires, theoretically:

Ce	85.45
C	14.54

We obtained the following figures:

	1.	2.	3.	4.	5.	6.
Cerium	86.46	85.99	85.37	85.74	86.12	85.93
Carbon	14.90	14.81	....	....	....	....

CONCLUSIONS.—In the electric furnace, cerium, in presence of carbon, gives a crystalline carbide having the formula CeC_2 analogous to calcium carbide and decomposed by cold water, forming a gaseous mixture of acetylene, ethylene and methane, and more or less condensed liquid and solid hydrocarbons.

H. Lanthanum Carbide

Preparation.—Lanthanum oxide is readily reduced by carbon at the temperature of the electric furnace. This reduction requires a higher temperature than that of cerium oxide. Lanthanum oxide is mixed with finely pulverized sugar carbon in the following proportions:

Lanthanum oxide	100
Sugar carbon	80

This mixture is packed in a carbon tube closed at one end and heated in the electric furnace for twelve minutes with an arc of 358 amperes at 56 volts.

Properties.—A well-fused, homogeneous mass is obtained which has a slightly darker color than cerium carbide. The pieces, examined under the microscope, are transparent and yellow-colored; they have a marked crystalline appearance. The density of crystalline lanthanum carbide was found to be 5.02 at 20°. It is thus slightly higher than that given by Petterson (4.71).

Fluorine does not attack lanthanum carbide, even if pulverized, at the ordinary temperature. If it is slightly heated, it burns brightly with the formation of fluoride.

Chlorine attacks the compound at 250° with evolution of light, forming lanthanum chloride. Bromine gives the same result at 255°. Iodine reacts similarly with evolution of light.

Lanthanum carbide burns in oxygen with more difficulty than cerium carbide. At redness, the combustion is complete, and this reaction affords the separation of lanthanum as oxide, and the total carbon as carbon dioxide.

Sulphur acts with difficulty on lanthanum carbide. The carbide can be heated in the vapor of sulphur to the temperature of the softening of glass without formation of a sulphide. The product treated with water gives a hydrocarbon and treated with hydrochloric acid it gives only very little hydrogen sulphide.

The vapor of selenium gives a more energetic action; selenide is formed which can be decomposed by hydrochloric acid with evolution of hydrogen selenide.

Nitrogen and phosphorus appear not to react between 700° and 800°. However, lanthanum carbide, which has been heated in nitrogen, gives a little ammonia with fused caustic potash.

Carbon dissolves in fused lanthanum carbide, and, on cooling, deposits as well-crystallized graphite.

Dilute acids readily attack lanthanum carbide while concentrated nitric acid is without action on it. On the contrary, hot, concentrated sulphuric acid is decomposed with formation of sulphurous acid. Lanthanum carbide, heated in a current of ammonia gas, is decomposed at redness with slight glowing, forming a nitride which, fused with caustic potash, gives ammonia. A nitride exists which we will study later. Hydrochloric acid gas attacks lanthanum carbide below redness, giving lanthanum chloride and hydrocarbons. The carbide heated below redness in a current of nitrous oxide or nitric oxide burns brightly.

Oxidizing agents, such as powdered permanganate, fused chlorate and nitrate of potassium attack it with great evolution of heat. Fused caustic potash destroys it with formation of hydrogen. Water rapidly decomposes lanthanum carbide at the ordinary temperature. Hydrated oxide is formed and hydrocarbon gases are evolved. The gas, thus produced, contains acetylene, ethylene and methane. The acetylene was absorbed by ammoniacal cuprous chloride, the ethylene by bromine, and the composition of the methane was ascertained by eudiometric analysis. In order to be certain that the latter gas was pure methane, it was treated

with absolute alcohol, free from air, according to Berthelot.[1] After separating the liquid, the vapor of alcohol was absorbed by sulphuric acid, and a new eudiometric analysis of the residue gave the same figures as before. We did not find a mixture of ethane and hydrogen, but only methane. We obtained the following results:

	1.	2.	3.	4.
Acetylene	71.75	70.18	71.17	70.71
Ethylene	1.93	1.15	0.95	2.01
Methane	27.22	28.67	27.88	27.98

These gaseous products contained nearly all of the carbon combined with the lanthanum.

An experiment was made on a definite weight of a carbide containing 5 per cent. of graphite. The gas obtained gave the figures in analysis No. 4. They correspond to 11.66 per cent. of carbon while, theoretically, we should obtain 13.7 per cent. This difference of carbon is found under the form of a small quantity of liquid and solid hydrocarbons, which can be separated by ether from the water used for the decomposition of the metallic carbide.

Analysis.—The total carbon was determined by direct combustion in oxygen. In another portion, a weighed amount of carbide was treated with dilute nitric acid, the graphite was weighed on a tared filter and the nitric acid solution evaporated and ignited gave the lanthanum.

	1.	2.	Theoretical LaC_2.
Lanthanum	85.42	85.80	85.23
Carbon	14.59	14.07	14.77

Conclusions.—Lanthanum oxide, mixed with carbon, and heated in the electric furnace, readily forms a transparent and crystalline carbide having the formula LaC_2. This carbide is decomposed by water at the ordinary temperature, giving a mixture of acetylene and methane with a small quantity of ethylene. The proportion of methane is a little greater than from cerium carbide.

When it is heated with water, the compound also gives a small quantity of liquid and solid hydrocarbons.

[1] Berthelot: "Méthode universelle pour réduire et saturer d'hydrogène les composés organiques," *Ann. chim. phys.*, 4e série, **20**, 392 (1870).

I. Carbides of Neodymium and Praseodymium[1]

In our work on the carbides of neodymium and praseodymium we used the pure oxides, which were kindly placed at our disposal by Demarçay, and by Chenal and Douiltut.

Preparation of Carbides of Neodymium.—Neodymium oxide, with which we started, possessed the dark color as shown by Demarçay; it corresponded to the formula Nd_2O_3. We prepared an intimate mixture of this oxide with sugar carbon in the following proportions:

	Grams.
Neodymium oxide	250
Sugar carbon	26

A small quantity of spirits of turpentine was added to this mixture, and it was compressed into small cylinders. The latter were gently heated in a porcelain crucible until combustible gases were no longer evolved. The product, while still hot, was placed in tight flasks and kept free from all moisture. This mixture was placed in a carbon crucible and heated for four minutes in the electric furnace with a current of 900 amperes at 50 volts. After the experiment, a fused mass was found in the crucible, which generally could be detached. In this case a nearly pure carbide of neodymium appeared. If it is heated too long the carbide of neodymium attacks the crucible, dissolves varying quantities of carbon and adheres to the sides.

Preparation of Carbide of Praseodymium.—The material used had a brown color and corresponded to the formula PrO_2. A mixture of this oxide with sugar carbon was treated in a similar manner to the previous one, but in the proportions:

	Grams.
Praseodymium oxide	250
Sugar carbon	32

The length of heating was the same and the product differed very little in appearance from neodymium carbide.

Properties.—Neodymium carbide, under the microscope, showed yellow hexagonal plates slightly darker than aluminum carbide. Its density is about 5.15. Praseodymium carbide has the same color and likewise possesses a crystalline appearance. Its density

[1] *Compt. rend.*, **136**, 595.

was found to be 5.10. The two carbides cannot be reduced by hydrogen at redness.

Fluorine produces no sensible action at the ordinary temperature, but when the carbide is slightly heated, light is evolved and the reaction continues in the current of fluorine gas. The fluorides obtained are insoluble in water. Neodymium fluoride is greenish white, while praseodymium is of a sulphur-yellow color. The heat of the reaction was sufficiently high to cause fusion; but the fluorides are not readily volatile.

In a current of chlorine gas the carbides do not react in the cold, but when heated to dull redness, light is evolved and the anhydrous chlorides are produced which are soluble in water with evolution of heat.

Bromine acts like chlorine, evolving light, while iodine vapor at dull redness evolves less heat, does not evolve light, and gives one or more iodides soluble in water.

If the carbides are heated to about 400° in a rapid current of oxygen, light is evolved and the oxidation is complete. This reaction was used for the determination of the carbon.

Sulphur slowly reacts at the boiling-point. The sulphides formed are readily decomposed by the acids, by boiling water, and slowly by cold water.

At 1200° nitrogen acts on the carbides, but the transformation into nitride is only superficial. The residue thrown into water gives ammonia. We shall see later that other experiments demonstrate the existence of nitrides, of neodymium and of praseodymium. Carbon rapidly dissolves in the fused neodymium and praseodymium carbides. On cooling, graphite separates. It is possible to obtain carbides of a gray appearance resembling plumbago. In contact with water, these carbides decompose as rapidly as the carbides of cerium, lanthanum and yttrium. They evolve large quantities of gas and leave a hydrated oxide. This hydrate is greenish white with neodymium, and purple with praseodymium. They also form liquid and solid hydrocarbons. The gas was analyzed by the method already described and was mainly formed of acetylene, with a small quantity of ethylene and of the ethylene hydrocarbons. It also contained methane hydrocarbons.

DECOMPOSITION OF NEODYMIUM CARBIDE BY WATER.

	1.	2.	3.	4.
Acetylene	66.22	65.42	65.80	67.20
Ethylene hydrocarbons	6.34	5.92	6.90	5.95
Methane hydrocarbons	27.44	28.66	27.30	26.85

DECOMPOSITION OF PRASEODYMIUM CARBIDE BY WATER.

Acetylene	67.50	68.31	....	....
Ethylene hydrocarbons	2.50	3.57	....	....
Methane hydrocarbons	30.00	28.12	....	....

The acid solutions of the two carbides behaved differently, according to the quantity of water which they contained. Concentrated nitric acid does not attack the carbides, while dilute nitric acid evolves a gas whose composition varies by reason of the oxidizing properties of the acid.

Similarly, boiling concentrated sulphuric acid is reduced with evolution of sulphur dioxide and the dilute acid acts on account of the water which it contains.

Hydrochloric acid gas does not act in the cold on these carbides, but at dull redness light is evolved. The products are soluble in water and with neodymium gives a rose solution, and with praseodymium a green solution.

The two carbides are attacked at redness without evolution of light by hydrogen sulphide with formation of a sulphide, the properties of which were the same as those of the one obtained by means of sulphur.

Ammonia gas acts at 1200° on the carbides of neodymium and of praseodymium. The former becomes black and the latter yellow. The residue, treated with water, gives hydrocarbons and evolves large quantities of ammonia, giving evidence of the existence of the nitrides of these metals.

Analysis.—The fused carbides were treated with dilute nitric acid, which dissolved them rapidly; when they contained a small quantity of graphite the latter was removed by filtration and its weight deducted. The nitrate was evaporated to dryness and ignited. From the weight of the oxide obtained, the quantity of metal contained in the carbide was calculated.

Other determinations were made by precipitating a slightly acid nitrate solution with ammonium oxalate. The oxalate was ignited

to oxide. In these determinations the figures were always lower.

The carbon was determined by combustion in oxygen, weighing as carbon dioxide. It is necessary that the combustion should take place at a high temperature in order that no unattacked carbide remains.[1]

CARBIDE OF NEODYMIUM.

	1.	2.	3.	Theoretical for NdC_2.
Neodymium	84.24	85.73	85.90	85.68
Carbon	14.08	14.28	13.37	14.32

CARBIDE OF PRASEODYMIUM.

	1.	2.	3.	Theoretical for PrC_2.
Praseodymium	84.60	85.10	84.91	85.41
Carbon	14.40	13.79	14.29	14.58

CONCLUSIONS.—Neodymium and praseodymium oxides, heated with carbon in the electric furnace, give crystalline carbides having the formula NdC_2 and PrC_2. These carbides are decomposed by cold water, giving a mixture of hydrocarbons and hydrogen, and hydrated oxide.

We have shown that the three alkaline earth carbides prepared in the electric furnace give pure acetylene; aluminum carbide under the same conditions gives pure methane. It is known that neodymium and praseodymium belong to the cerium group and in their properties are between the alkaline earth metals and aluminum. It is somewhat curious that the carbides of neodymium and praseodymium with water give a complex mixture of hydrocarbons, rich in acetylene and methane. We have observed that in the mixture of hydrocarbons the quantity of acetylene diminishes from cerium to neodymium and that neodymium and praseodymium, similar metals, that have for a long time been confounded under the name didymium, give with water a mixture of hydrocarbons of similar composition.

Finally, the carbides of cerium, lanthanum, neodymium and praseodymium all correspond to the formula RC_2.

J. Yttrium Carbide

The study of the carbides of yttrium and thorium was made with Etard.

Preparation of Yttria.—A number of minerals, such as gado-

[1] We took 143.6 for the atomic weight of neodymium and 140.5 for praseodymium.

linium, euxenite, monazite, contain the rare earths of the yttrium group. The usual method of treatment for the rare earths consists in attacking the powdered mineral with sulphuric acid and precipitating the oxides by oxalic acid.

The oxalates are washed, heated to 400° and then heated with dilute sulphuric acid. The clear solution is saturated with crystals of potassium sulphate. It is known that the double sulphates of the cerium group (lanthanum, didymium) are insoluble in a solution of potassium sulphate, while the double sulphates of the yttria group, such as erbium, holmium, etc., remain in solution. When these sulphate solutions no longer show the characteristic bands of neo- and praseodymium (old didymium), it is certain that the cerium and lanthanum are entirely precipitated. The mother-liquors are treated with oxalic acid, when all of the rare earths of the yttria group, erbium, holmium, thulium, etc., are obtained as oxalates. To separate the yttria from the other oxides, we used the following method: The complex mixture of the yttria earths is neutralized with sulphuric acid, then fractionally precipitated by neutral potassium chromate. Care should be taken to add only a small quantity of the alkaline chromate—about $^1/_{10}$ the necessary quantity. There is first formed a basic chromate of the rare earths, in which erbium, holmium and other elements predominate. The precipitate being basic, the solution becomes rich in chromic acid and takes on a beautiful color. The precipitate formed under these conditions immediately becomes crystalline. It is separated, washed, and reduced with acid and alcohol; the oxalate is then obtained which is ignited to oxide.

The red mother-liquors are treated again with another $^1/_{10}$ portion of potassium chromate; at the same time sufficient ammonia is added to effect neutralization, which is shown by the yellow coloration of the liquor. Another precipitate appears, at first flocculent, but soon becomes crystalline. On methodically continuing this operation, the tenth precipitate is basic yttrium chromate. The separated rare earth shows no absorption bands and its atomic weight is 89. With care it is possible to obtain these fractions in series by this

method, and with patience obtain hundreds of grams of yttria, free from the absorption bands of neodymium, praseodymium, erbium, holmium, thulium and samarium. This proceeding, more rapid than those hitherto described, furnished us the yttria used in our work.

Preparation of Yttria Carbide.—Very finely powdered yttria was intimately mixed with sugar carbon, and a small quantity of turpentine added to make a thick paste. The whole was strongly pressed and the blocks were heated in a Perrot furnace. This mixture was heated in the electric furnace in a carbon cylinder closed at one end. The reduction of the yttria by carbon takes place at a higher temperature than that of cerium oxide. With 900 amperes at 50 volts it is necessary to heat five or six minutes. During the reduction, metallic vapors are evolved which burn at the end of the tube with a white flame tinted purple. Yttrium and cerium give metallic vapors under about the same conditions as the alkaline earth metals.

Properties.—Yttrium carbide, YtC_2, appears in well-fused, brittle ingots with a distinct crystalline fracture. Under the microscope, yellow, transparent crystals, mixed sometimes with graphite, could be readily distinguished. The density of yttrium carbide in benzene at 18° is 4.13; Petterson found 4.18. We describe some new properties of yttrium carbide. Fluorine attacks it in the cold. It burns brightly in chlorine below dull redness. The reaction is similar in bromine vapor. Yttrium carbide burns with great ease in the vapor of iodine, forming a stable iodide. It burns in oxygen, in the vapor of sulphur, and in that of selenium.

Concentrated acids act only with difficulty. Sulphuric acid in the cold gives no evolution of gas, while heated gives sulphurous acid. Water decomposes it in the cold, giving a white hydrated oxide and a mixture of hydrocarbons of the following composition:

	1.	2.
Acetylene	71.7	71.8
Methane	19.0	18.8
Ethylene	4.8	4.45
Hydrogen	4.5	4.95

The relative quantities of the different hydrocarbons are some-

what similar to those given by cerium carbide. Acetylene predominates and hydrogen is found in small quantities.

Analysis.—The method of analysis used in this work has been described previously with cerium carbide. We obtained the following results:

	1.	2.	Theoretical for YtC_2.
Yttrium	78.5	78.72	78.76
Carbon	21.4	21.55	21.23

K. Thorium Carbide

Preparation of Thorium Oxide.—Thorium oxide is obtained from thorite or its richer variety, orangite. These minerals are hydrated silicates of thorium containing iron, lime, the rare earths of the cerium group (lanthanum, didymium) and those of the yttrium group (erbium, etc.).

The pulverized mineral is treated with boiling hydrochloric acid. The solution containing the metallic chlorides is precipitated by oxalic acid; the thoria and the rare earths come down in the acid solution. It is washed to remove the iron, calcium and magnesium. The mixture of these oxalates is treated with a saturated solution of ammonium oxalate, which possesses the property of dissolving thorium oxalate without acting on the properly called rare earths. The filtered liquid, treated with nitric acid, separates thorium oxalate. This solution and precipitation is repeated until the earth is entirely pure.

This thorium oxide in a 20 per cent. solution shows, with the spectroscope, no absorption in a length of 20 cm. It is entirely white; the atomic weight of the thorium corresponds to 232. Finally, if brought on an incandescent wick, it gives only a weak light of a lilac color. It is known to-day that this is the most sensitive reaction for pure thorium.

Preparation of the Carbide.—Troost[1] obtained in the electric furnace a fusion of thorium which had the composition approaching the formula ThC_2. This fusion possessed the property of effloresing in contact to moist air. To obtain crystalline carbide, we heated in the electric furnace a mixture of 72 grams of thorium

[1] Troost: "Sur la préparation du zirconium et du thorium," *Compt. rend.*, **116**, 122 (1893).

oxide and 6 grams of carbon pressed into small cylinders, such as we used for yttria. With a current of 900 amperes at 50 volts the reduction is accomplished in four minutes.

Properties.—Pure thorium carbide, ThC_2, appears as a fused, homogeneous mass having a crystalline fracture and a good cleavage. Under the microscope it is seen to be formed of small, yellow, transparent crystals, mixed with flakes of graphite. The density of thorium carbide at 18° is 8.96. The action of the halogens on this compound is similar to that which they exert on yttrium carbide. Slightly heated thorium carbide burns in oxygen with dazzling brightness. Heated in the vapor of sulphur it burns brightly, leaving a dark-colored sulphide which is attacked by hydrochloric acid, and which distinguishes this compound from that described by Chydenius.

In selenium vapor it burns brightly below redness, forming a selenide which is attacked by dilute hydrochloric acid with evolution of hydrogen selenide. Hydrochloric acid gas attacks thorium carbide at dull redness with evolution of light, forming a difficultly volatile chloride.

With hydrogen sulphide the decomposition is slow and without evolution of light. Heated in ammonia gas to 500°, thorium carbide evolves hydrogen and the residue, treated with fused potash, gives ammoniacal vapors. Thorium nitride is formed.

Concentrated acids have little action on this compound, while dilute acids rapidly attack it. Fused potash, chlorate and nitrate of potassium decompose the carbide with evolution of light. Thorium carbide introduced into cold water decomposes, giving a gaseous mixture which, on analysis, gave the following results:[1]

	1.	2.
Acetylene	47.05	48.44
Methane	31.06	27.69
Ethylene	5.88	5.64
Hydrogen	16.01	18.23

Moreover, we observed the formation of a small quantity of liquid and solid hydrocarbons.

[1] The acetylene was determined with ammoniacal cuprous chloride. The residue treated with bromine gave the content of ethylene. Eudiometric combustion of the remaining gas showed it contained a mixture of the hydrocarbons C_nH_{2n+2} and hydrogen. In case of hydrogen, the gas was treated with boiling alcohol, the vapors of the alcohol were removed by boiling sulphuric acid, and finally a eudiometric combustion was made of the residue which was pure hydrogen.

Analysis.—We obtained the following figures:

	1.	2.	Theoretical for ThC_2.
Thorium	89.70	89.53	90.62
Carbon	10.30	10.47	9.37

Yttrium, as shown by Petterson, gives a carbide having the formula YtC_2. This carbide can be obtained in transparent crystals, which decompose cold water with the formation of a gaseous mixture rich in acetylene, containing methane, ethylene, and a small quantity of hydrogen. Thorium similarly gives a transparent crystalline carbide having the formula ThC_2 which in presence of water also gives gaseous hydrocarbons containing less acetylene and more free hydrogen.

L. Magnesium Carbide

By carefully heating powdered magnesium in a current of acetylene gas (reaction shown by Berthelot), an impure magnesium carbide is obtained, which is mixed with carbon, but with cold water evolves acetylene gas.

This magnesium carbide was placed in a double crucible of pure graphite and heated in a carbon tube closed at one end, with a current of 600 amperes at 60 volts. Length of heating, six minutes. After cooling, the black substance remaining in the tube gave no evolution of gas with water. Magnesium carbide is completely decomposed at this high temperature. This explains why it is possible to fuse magnesium and bring it into a liquid state in a carbon crucible, without reduction of the oxide. At the melting-point of magnesia, magnesium carbide cannot exist.

M. Aluminum Carbide

Heretofore no combination of carbon and aluminum has been known. The solubility of carbon in aluminum has been doubted by many investigators.[1] We have been able to prepare a crystalline aluminum carbide having the formula Al_4C_3.

Preparation.—To obtain this compound, the electric furnace for tubes described in the beginning of this work is used. Sufficiently thick carbon boats, filled with aluminum, are placed in the carbon

[1] According to Mallet, aluminum does not combine with carbon; on the contrary, Franck, by heating a mixture of lampblack and aluminum, obtained a metal which, with hydrochloric acid, gave hydrogen mixed with acetylene.

tube through which a current of hydrogen passes. Each boat contains about 15 or 20 grams of aluminum. They are heated from five to six minutes with a current of 300 amperes at 65 volts. The cooling is completed in a current of hydrogen and the boats are found to be filled with a gray-colored metallic mass on the surface of which are metallic spheres which form on account of the increase of volume at the moment of solidification. When the contents of the boat are broken, the aluminum appears to be mixed with bright yellow crystals.

Aluminum having the same appearance is obtained on moderately heating the metal in a carbon crucible in the electric furnace; only in the latter preparation the yellow crystals of aluminum carbide are contaminated with a small quantity of nitride. On reducing in the electric furnace a mixture of kaolin and carbon, the result is similar. Copious vapors are evolved and there remains a metallic fusion which has a good crystalline fracture and pale yellow color. To separate the carbide from the excess of the metal, the fusion is broken into pieces of from 1 to 2 grams and treated in portions of not more than 2 or 3 grams with concentrated hydrochloric acid. This treatment is carried out in a test-tube cooled by ice-water. It is important to keep the temperature low and to work as rapidly as possible, as even cold water, as we shall see later, decomposes aluminum carbide.

When the action ceases by reason of the formation of aluminum chloride, which is only slightly soluble in hydrochloric acid, it is washed with ice-water, the liquid decanted and the metal treated with a fresh quantity of acid. As soon as no more hydrogen is evolved, the residue is rapidly washed with cold water, then with absolute alcohol, finally with ether and dried in the air-bath. In order to obtain a good preparation, the treatment should be completed in thirty minutes. A series of test-tubes are used and all are worked together. Less concentrated hydrochloric acid gives a less violent action, but takes longer and gives an altered product.

Properties.—Aluminum carbide prepared under the conditions described appears in beautiful, yellow, transparent crystals, some of which attain a diameter of 5 to 6 mm. Some of the crystals

have an angular hexagonal form and are somewhat thick. Their density in benzene is 2.36. They are only decomposed at the highest temperature of the electric arc. Chlorine attacks the carbide at low redness with evolution of light. Aluminum chloride is formed and flakes of carbon remain which preserve the form of the original crystals; the carbon is amorphous and contains no graphite. Bromine is without action on the carbide at the ordinary temperature, but at about 700° light is evolved; aluminum bromide is formed along with a residue of carbon. Iodine appears to be without action at bright redness.

Oxygen, at dull redness, only attacks the carbide on the surface, due to the alumina which is formed at the beginning of the reaction, covering the carbide with a protecting layer. On the contrary, sulphur attacks it at the same temperature with great evolution of heat. In a short time aluminum sulphide and a little carbon bisulphide are formed. The greater part of the carbon remains as black flakes.

Nitrogen and phosphorus do not decompose aluminum carbide at a dull red heat.

Certain oxidizing agents attack the carbide energetically. Mixed with dry potassium permanganate and slightly heated, it takes fire, alumina is formed, and carbon dioxide is evolved. Potassium bichromate and chromic acid burn it slowly at low redness. Lead dioxide and litharge are reduced with evolution of light, while potassium chlorate and nitrate are without action. A solution of alkaline bichromate, to which sulphuric acid has been added, attacks it slowly in the cold and at the boiling temperature. Fuming nitric acid is without action in the cold or warm, but the addition of a small quantity of water causes action to be produced in a short time. Concentrated hydrochloric acid only attacks the carbide very slowly, while the dilute acid dissolves it after some hours. Boiling concentrated sulphuric acid is reduced with the formation of sulphurous acid; the dilute acid acts at about 100°.

Fused potash attacks the carbide very energetically at about 300°; on the contrary, the alkaline carbonates, at bright redness produce only an incomplete decomposition. The most curious reaction of this carbide is the slow decomposition of water produced

at the ordinary temperature. We have previously shown that the crystalline alkaline earth carbides of the formula CaC_2 are decomposed by water, giving pure acetylene gas. Yellow aluminum carbide having the formula Al_4C_3 is decomposed by water, giving methane CH_4. Crystals of the compound and a small quantity of water are best introduced into a tube containing mercury in order to observe this decomposition. After twelve hours, 0.145 gram of this carbide gave 7.5 cc. of gas and after seventy-two hours 35.5 cc. To be complete the decomposition requires ten to twelve days. Heat accelerates the action, but light appears to be without effect.

This reaction, according to our analyses, is expressed by the equation:

$$Al_4C_3 + 12H_2O = 3CH_4 + 2Al_2(OH)_6$$ [1]

Analysis.—The analysis of aluminum carbide presented numerous difficulties on account of its ready decomposition by water. If the samples obtained are not absolutely pure, they contain aluminum hydroxide, which complicates the determination. The formula Al_4C_3 requires Al, 75.4 and C, 24.6.

Estimation of Aluminum.—We used two methods to determine the aluminum.

(1) A known weight of the carbide is left for some hours in contact with dilute hydrochloric acid, until complete solution takes place. If the substance is absolutely pure, there is no residue; otherwise it can be filtered to remove the small quantity of carbon and insoluble products. The clear liquid contains aluminum chloride; it is slowly evaporated, then carefully ignited. Only alumina remains, the weight of which gives the quantity of aluminum contained in the compound. We thus found:

	1.	2.
Aluminum.....	74.48	75.12

(2) A definite weight of the aluminum carbide is treated with potash in a silver crucible. The residue is taken up in water and

[1] According to this equation 0.100 gram of carbide should give 48.8 cc. of methane. The result of two experiments was:

1. 0.070 gave 31.5 cc.; theoretical, 32.6.
2. 0.145 gave 69.1 cc.; theoretical, 70.90.

The gas obtained under these conditions is methane, as shown by the following analysis; Original volume, 1.6 cc.; oxygen added, 8.5 cc. After explosion, 7.1 cc.; contraction, 3 cc. After action of potash, 5.6 cc.; carbon dioxide formed, 1.5 cc.

the solution neutralized with hydrochloric acid which is kept in slight excess. The liquid is diluted, and the boiling solution treated with sodium thiosulphate. A precipitate of alumina and sulphur is obtained. After filtration, it is ignited and weighed.

	1.	2.	3.
Aluminum	74.7	74.9	75.7

Determination of the Carbon.—When aluminum carbide is treated with chlorine the metal is completely removed as chloride, while carbon remains. It is easy to remove the excess of chlorine retained by the carbon, by heating the latter in a current of hydrogen. The carbon is then burned in oxygen and the carbon dioxide formed is weighed. This method gave us low results. This was true with perfectly dry chlorine. It appears that chlorine can contain a small quantity of oxygen and carbon dioxide and form a small quantity of alumina which frequently contaminates the product. This mixture of alumina with carbon is attacked by chlorine with formation of carbon monoxide. The best figure that we obtained by this method was 23.5, while the formula Al_4C_3 requires 24.6.

The only method that gave concordant results consisted in the decomposition of water, at the ordinary temperature, of a definite weight of the carbide and measuring the volume of methane gas evolved. From the latter, the weight of the carbon contained in the aluminum carbide is readily calculated. We thus found:

	1.	2.	3.
Carbon	24.2	24.7	24.8

Conclusions.—Carbon can unite with aluminum to form a yellow crystalline carbide having the formula Al_4C_3. This compound possesses marked reducing properties; its most curious reaction is the slow decomposition of water at the ordinary temperature with evolution of methane. This is the first example of this kind of decomposition. Possibly this carbide takes part in geological phenomena which, during centuries, produce methane.

N. Glucinum Carbide

Glucinum carbide was obtained by Lebeau[1] by heating a mixture of glucina and carbon. The carbon used was sugar carbon

[1] Lebeau: *Compt. rend.*, **121**, 496.

and the glucina was obtained by the treatment of beryl in the electric furnace.

(1) *Treatment of Beryl.*[1]—The treatment depends on the fact that when beryl is strongly heated in the electric furnace (950 amperes at 45 volts), it loses silica. By prolonging the heating in presence of carbon, it is possible to obtain total reduction; the most of the silica distils and a fused metallic mass remains which contains a mixture of aluminum and glucinum carbide, and iron and carbon silicides. This substance, treated with dilute acid, gives a solution which contains the glucina and alumina. If hydrofluoric acid is used, the first treatment gives a sufficiently pure glucinum solution, aluminum fluoride remaining insoluble. By substituting for the carbon, a more powerful reducing agent, such as calcium carbide, better results are obtained from the standpoint of extraction of glucina.

Fifty kilos of beryl and fifty kilos of coarsely powdered calcium carbide were placed in a calcium carbide furnace and heated an hour and a half with a current of 1500 amperes. At the end of this time a fused mass of 31.5 kilos was obtained; the rest of the substance had not been heated sufficiently high.

The fused mass was crushed and allowed to remain in moist air. when it crumbled. In this alteration product the glucinum and aluminum were as hydrated oxides or carbides not yet decomposed, and were easily attacked by reagents. It is possible to remove considerable glucina by digestion with a saturated ammonium carbonate solution, but this treatment requires prolonged action. The use of sulphuric or hydrofluoric acid permits the rapid extraction of from 90 to 95 per cent. of the glucina contained in the beryl.

(2) *Preparation of Glucinum Carbide.*—An intimate mixture of pure glucina is made with half its weight of sugar carbon. This mixture is incorporated with a little oil, then pressed into small cylinders, and heated to dull redness. These cylinders are heated in a furnace for tubes with a current of 950 amperes at 40 volts (a weaker current gives a product containing nitrogen). When the experiment is successful, the tube is found to contain fused masses covered with graphite, having a crystalline fracture, and a reddish coloration. This product contains no nitrogen and is a

[1] Lebeau: *Compt. rend.*, **126**, 1202.

definite carbide, containing no other impurities than a small quantity of graphite. The chemical properties of this carbide much resemble those of aluminum carbide. One of its most characteristic reactions is its decomposition by water at the ordinary temperature with formation of hydrated glucina and methane gas. This reaction is very slow in an acid liquor; on the contrary, it is rapid and complete in a hot, concentrated solution of soda or potash. In the latter case, a soluble combination of glucina with the alkali is formed which facilitates the reaction.

Analysis.—The analysis of the glucinum carbide was made by treating the substance either with chlorine gas, with fuming nitric acid, or with a concentrated solution of soda or potash (which permits the determination of the methane). The following figures were thus obtained:

	1.	2.	3.	4.
Glucinum	59.53	59.17	60.91	59.76
Carbon	40.47	40.83	39.09	40.24

Taking 13.8 for the atomic weight of glucinum, the formula Gl_4C_3 requires: Gl, 60.52; C, 39.47.

O. Iron Carbide

For a long time the study of iron carbide has attracted the attention of chemists. We cite particularly the work of Sir F. Abel, Deering, Müller, Osmond and Woerth (1885), Obenolds and Read (1894), the work of Mylius, Foerster and Schwenz (1896) which is a model for patient work and regular experimentation, that of Campbell (1896) who more particularly studied the decomposition of iron carbide by dilute hydrochloric acid and the production of gaseous and liquid hydrocarbons, and the work of Züptner (1896) on the saturation of iron with carbon. There are, besides, a number of other publications on the same subject.

In all of these investigations it is seen that melted or annealed steel contains a definite carbide corresponding to the formula Fe_3C, which can be readily prepared.

Blast-Furnace Sows.—In our first experiments we studied some sows of the blast-furnace in which different authors have mentioned the formation of definite carbides of iron and attributed various formulas to them. (1) We first studied a sow from a

blast-furnace in Denain presented by Maurice Meteyer, Engineer of the Society of Denian and Anzin. This fused, crystalline mass was obtained from the bottom of blast-furnace No. 2. One specimen, which was several centimeters across, at first sight appeared crystalline, but on closer examination it was observed that the dihedral angles showed no regularity. The edge and faces were more or less curved. The analysis of a sample gave the following results: Iron, 87.99; total carbon (combined carbon and graphite), 8.75; silicon, 2.17. On repeating the analysis on different portions of the same piece, it was seen that the carbon content varied considerably. These pseudo-crystals were all formed by pressure of the fused mass between the large flakes of graphite; they did not correspond to any definite formula.

The insoluble residue, after destroying the graphite, did not contain diamond.

(2) The second product which was studied was from Fromholt. It was from the firm of Metz & Co. d'Esch-sur-l'Alzette (Grand duche 'de Luxembourg), and came from the crucible of blast-furnace No. 33.

Specimen A.—This specimen was in compact non-homogeneous pieces from a crystalline portion of the product and contained very little cast iron. By treatment with hydrochloric acid, the substance was completely attacked; a large residue remained which was partly transparent and was rich in graphite. It was alternately treated with hydrofluoric and sulphuric acid and the graphite destroyed by potassium chlorate and nitric acid. A little residue remaining after this treatment was fused with potassium bisulphate, then with potassium acid fluoride and finally treated with boiling sulphuric acid. After all of these treatments, nothing remained that could be seen with the microscope. The residue did not contain the diamond.

Specimen B.—Specimen of 58 grams of a non-homogeneous substance containing purple crystals of titanium nitride, octahedral crystals of titanic acid, and other yellow and black crystals in fused masses of which little was metallic. The composition of the metal corresponded to no definite formula. After the above treatment we could find nothing remaining, with the microscope.

Specimen C.—A piece of 42 grams gave no diamond. The specimens were particularly interesting, inasmuch as it was in the product from d'Esch-sur-l'Alzette that Russel found the transparent diamond. Our specimens contained none.

Iron Carbide.—When Swedish iron or pure iron[1] is fused in presence of sugar carbon in the electric furnace, the fluidity becomes less and less as the temperature raises. At a temperature close to the melting-point of titanium, the contents of the carbon crucible become so viscous that it can be inverted without anything running out. Later, when the temperature falls, the metal becomes liquid and flows like water. When the mass cools, a fusion of cast iron is obtained which is covered with graphite and shows all the characteristics of gray iron. If the cold metal is studied, especially that from the pure iron, it is found to contain only very little combined carbon—about 1 per cent. The metallic mass contains numerous crystals of graphite.

Nickel, which also dissolves a large quantity of carbon at a high temperature, shows the same reaction. The metal cooled slowly in the air contains only a little combined carbon.[2]

On treating the fusion with dilute acid, a large part of the carbon escaped as hydrocarbon gases, while the rest remained as the more or less complex forms which have been poorly studied. When we prepared transparent or crystalline diamond by suddenly cooling cast iron in water, we observed that in the center of the metal radiating masses frequently appeared, which had the appearance of the boride or silicide of iron, compounds which are perfectly definite and crystalline. We thought that iron carbide can possibly exist at a very high temperature and be almost entirely destroyed by again descending to the melting-point of cast iron. Similar examples of decomposition are known in chemistry. It was thus that Henri Sainte Claire Deville and Debray showed by rapidly cooling the vapor given off by boiling silver in contact with the air that the metallic silver collected contains silver oxide. Silver oxide is formed at a higher temperature than its decomposition point.

[1] This iron was prepared by reduction of the oxide in a current of hydrogen.

[2] Two specimens of nickel, on analysis, gave 0.21 and 0.23 per cent. of combined carbon, and the metal remained malleable.

Similarly Troost and Hautefeuille showed that ozone, which is destroyed by a slight elevation of temperature, can be produced between 1300° and 1400°. We consider that the direct preparation of iron carbide is another example of this curious phenomena. In reality, if we rapidly cool an iron saturated with carbon we obtain a metallic fusion rich in iron carbide. Its content of iron can be 5.25 per cent.

Preparation of Iron Carbide.—With the view of obtaining a pure carbide, complete saturation of the fusion should be avoided and the formation of graphite should be prevented. To this end, 500 grams of Swedish iron are heated in the electric furnace in a carbon crucible which gives the necessary carbon. The heating lasts three minutes with a current of 900 amperes at 60 volts. While the furnace is in operation, the crucible is grasped with the pincers and dipped in a vessel filled with cold water. This is a repetition of the experiment which served to produce the diamond, only in this preparation, whether the fusion is well or poorly united, or whether pressure exists or not, carbide is always formed.

The fusion which is obtained is very hard and brittle, and frequently shows a remarkable crystalline appearance. It contains no graphite and 3 to 4 per cent. of combined carbon.[1]

To separate the crystals of iron carbide appearing in the metal, we used the method of Mylius, Foerster and Schwenz in their work on the carbide in steel, modifying it in order to obtain a pure product.

(1) Two fusions of the cast iron were placed in a crystallizing dish containing a 7 per cent. solution of hydrochloric acid and connected with the positive poles of two Bunsen cells, each cell to one fusion. The two negative poles were connected with a vertical carbon plate, placed in the corner of a crystallizing dish.

At the end of twenty-four hours, the fusions were removed and the friable part taken out, and it consisted of a complex mixture containing the carbide and amorphous carbon.

(2) Pieces of the fusion were placed in a narrow glass tube in contact with very dilute[2] acid for three weeks and out of air contact.

[1] This fusion gave the following figures : Combined carbon, 3.31, 3.49, 3.68, 3.92.

[2] Sulphuric acid, 9.8 per cent.; hydrochloric acid, 7 per cent.; acetic acid, 6 per cent.

(3) When only a little carbide is desired at one time, it is possible to use stronger acid and work in the warm. Iron is, in general, more easily acted on than the carbide; the latter remains as a residue by careful treatment with mineral or organic acids, iodine water, chromic acid, etc.

Normal nitric acid[1] acts on the finely pulverized solution, giving the carbide mixed with a small quantity of light carbon. Semi-normal nitric acid after several hours gives a nearly pure carbide.

Purification.—Whatever method is used, the carbide obtained is contaminated with a variable quantity of free carbon and liquid or solid hydrocarbons which are scarcely soluble in ether. It is possible to obtain a pure compound corresponding exactly to the formula Fe_3C by treating the impure carbide with fuming nitric acid as free as possible from water. The carbide of iron is not attacked in the cold and it is not decomposed by the boiling acid. On allowing the carbide to remain for two hours in fuming nitric acid at 35°, the free carbon and the hydrocarbons dissolve. The mixture is poured into a large excess of water, the latter removed by decantation, and the substance washed with alcohol, then with ether, and dried in carbon dioxide at 100°, care being taken not to remove the carbide from the gas until it is completely cold. The purification of the iron carbide can be hastened by the addition of a small quantity of potassium chlorate to the nitric acid. A 10 per cent. aqueous solution of chromic acid can also be substituted. In the latter case the solution is boiled until the crystals become bright.

Properties.—The carbide which corresponds to the formula Fe_3C, as we shall see later, has the appearance of the product obtained from steel, but appears in more voluminous crystals. It has a bright white color, and contains broken crystals along with some of more regular form. Its density is 7.07 at 16°. It is not attacked in the cold by dry oxygen, but moist air containing carbon dioxide decomposes it somewhat rapidly. Heated in oxygen it burns more or less rapidly, depending on its state of division. In very fine powder it takes fire in air below 150°. It evolves light in sulphur vapor at about 500°. It burns brightly in chlorine below 100°. It evolves light at about 100° in the vapor of bromine,

[1] The normal nitric acid contains 1 molecule per liter or 60 grams per liter of solution.

while the vapor of iodine attacks it only at redness and without evolution of light.

Hydrochloric acid gas attacks it at about 600°, forming ferrous chloride and hydrogen, which contains a small quantity of hydrocarbons.

Fuming nitric acid does not attack the carbide in the cold even if finely divided, nor even in contact with platinum. But the addition of a small quantity of water is sufficient to produce decomposition.

All of the dilute acids more rapidly attack the iron than the carbide. With boiling acids the action rapidly becomes complete.

Dilute hydrochloric acid, heated in a sealed tube with iron carbide, gives hydrogen and methane: H, 86.33 cm.; CH_4, 13.37 cm. Under the same conditions, concentrated acid gave: H, 73.35 cm.; CH_4, 26.35 cm. Pure water does not act on iron carbide between 0° and 150°; the same is true of saturated solutions of sodium chloride or magnesium chloride.

In general, its properties resemble those of the carbide obtained from steel.

Analysis.—Carbide obtained by electrolysis.

	1.	2.	3.	Theoretical.
Iron	93.40	93.22	93.14	93.33
Carbon	6.47	6.67	6.67	6.66

Carbide obtained by iodine water.

	1.	2.
Iron	93.10	93.25
Carbon	6.66	....

Carbide obtained by dilute acids.

	1.	2.
Iron	93.17	93.46
Carbon	6.58	6.61

Conclusions.—When pure iron and sugar carbon are heated to the high temperature of the electric furnace, on slowly cooling the fusion, only a very small quantity of combined carbon is found in the metal. A gray cast iron is obtained which solidifies at about 1150°. If the metal at 1300° to 1400° is cooled in an ingot mold it contains graphite and a large quantity of combined carbon, or is white iron. Finally, if iron saturated with carbon at 3000° is sud-

denly cooled in water, a crystallization is produced in the metal, and it is possible to separate a pure and definite crystalline iron carbide, having the formula Fe_3C. This carbide is identical with that from the steel.

All these facts can be explained by assuming that iron carbide, like ozone and silver oxide, is formed at a very high temperature, then gradually decomposes by lowering the temperature. A considerable quantity is found in steel whose fusion-point is high and very little is found in gray iron. In all of our experiments we have not considered the formation of the carbide in the liquid metal.

P. Manganese Carbide

In the thermal investigations that Troost and Hautefeuille made on the carbides of iron and manganese, these workers mentioned manganese carbide, Mn_3C, which is prepared in the wind-furnace and which, on slow cooling, gives a cleavable solid.[1]

We obtained the same compound in the electric furnace and have studied its decomposition by water.

Preparation.—To obtain the carbide, a mixture of sugar carbon and pure Mn_3O_4 are heated in the following proportions: Manganese oxide, 200; sugar carbon, 50. It is well to make the reduction in a carbon tube closed at one end on account of the great volatility of manganese at the temperature of the electric furnace. With a current of 350 amperes at 50 volts, the heating requires five minutes; with 900 amperes at 50 volts, the reduction is almost instantaneous.

Properties.—The carbide, allowed to remain in the air for several days, rapidly crumbles, as Troost and Hautefeuille have shown. Its density is 6.89 at 17°. Cold fluorine attacks it with evolution of light, giving a violet fluoride which we expect to investigate further. Chlorine decomposes it at a lower temperature and as soon as glowing commences, it continues to burn throughout the mass. Slightly heated, it burns in oxygen as well as in nitrous oxide and nitric oxide. Ammonia gas acts on manganese carbide at low redness, setting free hydrogen and forming a metallic nitride.

[1] Troost and Hautefeuille: "Sur les fontes manganésifères," *Compt. rend.*, 80, 909 (1875).

Dilute acids readily attack manganese carbide; hydrochloric acid in particular gives liquid hydrocarbons, an analogous reaction to that studied by Cloëz with cast iron.

Hydrochloric acid gas, below redness, gives manganese chloride with evolution of hydrogen containing a small quantity of gaseous hydrocarbons.

The action of water on this carbide was of particular interest to us. When the carbide is placed on a mercury bath in presence of an excess of water, the latter is decomposed with formation of a white hydrated oxide and production of a gas which burns with a slightly luminous flame.

The analysis of this gaseous body showed that it contained neither acetylene nor ethylene and that it consisted of a mixture of methane and hydrogen. By using carbides more or less rich in carbon and prepared at more or less elevated temperatures, eudiometric combustion gave the following figures:

	1.	2.	3.
Methane	51.00	51.32	50.60
Hydrogen	49.00	48.68	49.40

When the carbide contains an excess of metallic manganese the latter decomposes water and a larger quantity of hydrogen is obtained. One such specimen[1] gave, in fact, the following figures:

Methane	43.57
Hydrogen	56.43

The carbide, saturated with carbon, always gives about the same ratio of methane and hydrogen. Liquid or solid hydrocarbons are not found in the water which was used for the decomposition.

On weighing the carbide taken in the experiment, and measuring the gas evolved, it has been possible to establish the following formula for the reaction.[2]

$$Mn_3C + 6H_2O = 3Mn(OH)_2 + CH_4 + H_2.$$

Analysis.—The estimation of the carbon, taking into account

[1] This manganese carbide was prepared in the wind-furnace.

[2] We decomposed by water 0.585 gram manganese carbide containing 2.3 per cent. of graphite which makes only 0.5726 gram of the carbide Mn_3C. At 761 mm. pressure and a temperature of 12° we obtained a gas volume of 136 cc., which contained 51 per cent. methane, or 69.3 cc. reduced to 0° and 760 the volume became 66.17 cc. It contained 0.0354 per cent. of carbon. According to the above formula there should have been obtained 72.4 cc. of methane, that is to say, 0.0388 per cent. of carbon, a figure close to that which we found. The experiment then verifies our equation.

the graphite contained in the compound and the estimation of the manganese, have given the following figures (Mn = 55):

	1.	2.	Theoretical for Mn_3C.
Manganese	93.5	93.22	93.23
Carbon	6.5	6.78	6.77

CONCLUSIONS.—The carbide Mn_3C discovered by Troost and Hautefeuille can be formed between 1500° and 3000°. When it is pure, it decomposes water at the ordinary temperature, giving a mixture of equal parts of methane and hydrogen. This reaction is produced according to a very simple equation.

Q. Uranium Carbide

Uranium oxide technically prepared contains, as impurities, a small quantity of iron and an appreciable quantity of alkali metal. In reality it is a variable combination of uranium oxide with soda, potash or ammonia.

The commercial oxide is brought into solution with pure nitric acid and the salt obtained is submitted to two successive crystallization; the crystals are dissolved in ether (method of Péligot),[1] and the mixture is dissolved on the water-bath after having added an additional volume of water. This distillation is effected in a glass apparatus. Water is added to avoid the violent reaction which is produced at the end of the reaction with projection of a part of the liquid by reason of the sudden evolution of red vapors.

The aqueous solution of uranium nitrate is evaporated to dryness. The residue after ignition is yellow uranium oxide. A second roasting for two hours in the Perrot furnace converts it into the green oxide which is used in the preparation of the carbide.

Preparation.—The green oxide of uranium is mixed with finely powdered sugar carbon in the following proportions:

	Grams.
Uranium oxide	500
Sugar carbon	60

The mixture (about 800 grams), placed in a carbon crucible, is heated in the electric furnace for eight to ten minutes, with a current of 900 amperes at 50 volts. About five minutes after the beginning of the experiment, reduction takes place and bright

[1] Péligot: "Recherches sur l'uranium," *Ann. chim. phys.*, 3e sérei, **5**, 7 (1842).

sparks escape from the furnace. Some minutes later the sparks disappear and there remains in the crucible a liquid carbide of uranium which is allowed to solidify and cool in the furnace.

Properties.—This carbide appears in the form of heavy pieces with a metallic appearance, and with a crystalline fracture resembling bismuth in color. It is more or less rich in graphite, coming in part from the carbon of the crucible. The pieces examined under the microscope are distinctly crystalline, brightly reflecting and sometimes show square faces. Its density taken at 18° in benzene is 11.28. It is not very hard; it scratches glass and quartz, but not corundum; struck with a hard body, it gives bright sparks like metallic uranium. Pulverized in an agate mortar, without care, it takes fire and continues to burn.

Fluorine, in the cold, is without action on it, but slightly heated, it burns brightly in the gas. Chlorine attacks it at 350° with evolution of light, giving volatile uranium chloride.

Bromine acts at 390°, giving a faint light. Iodine attacks it without appearance of light below redness. With the latter element, uranium carbide gives a slightly volatile, coherent mass which is soluble in water with a green color.

Uranium carbide burns brightly in oxygen at 370°, and when the reaction begins at one point it proceeds throughout the mass without further heating. A large amount of carbon dioxide is given off and there remains a violet-black oxide which gives a green streak on porcelain. With fused potassium nitrate or chlorate it takes fire, forming alkaline uranate.

Uranium carbide burns in sulphur vapor with evolution of light, at the temperature of fusion of glass; uranium sulphide and carbon bisulphide are formed.

Selenium acts at a lower temperature than sulphur. The light is bright, and uranium selenide is formed.

Nitrogen attacks uranium carbide at 1100°, but the transformation into nitride is incomplete. The residue treated with potash gives ammonia. At 370° in nitric oxide, uranium carbide takes fire and leaves a black residue of complex composition.

Dilute hydrochloric, sulphuric and nitric acids attack it slowly in the cold, giving with the first a green solution and with the last a yellow.

The concentrated acids, except nitric, act with difficulty in the cold. On the contrary, when hot, the decomposition is rapid.

Hydrochloric acid gas acts at 600° with evolution of light. A chloride is formed which, with water, gives a brown, unstable solution. Hydrogen sulphide, at the same temperature, gives a uranium sulphide.

Ammonia gas at redness gives a nitride; the transformation is not complete.

The most curious reaction presented by this compound is its action on water. When pieces of uranium carbide are brought in contact with water at the ordinary temperature, it slowly evolves gases, and the action increases if the quantity of water is small or if the temperature is slightly raised. When the reaction takes place in absence of air, there is formed at the same time a green hydroxide of uranium. In contact with the air, this oxide takes on a dark gray color, almost black. The gas evolved by uranium carbide is not a single hydrocarbon, but a mixture of hydrocarbons and hydrogen. Submitted to analysis, it gave the following composition:

	1.	2.
Acetylene	0.17	0.72
Ethylene	6.77	5.16
Methane	78.05	80.60
Hydrogen	15.01	13.52

There is thus obtained a complex mixture of hydrocarbon gases, and if the carbon thus obtained is summarized from a given weight of uranium carbide, it is seen about how much is lost in two series of weights of carbon which entered into combination with the uranium. Since the decomposition was complete we extracted the water which had been used in the reaction with pure ether. On distilling the ether, we obtained all the lacking carbon as a mixture of liquid and solid hydrocarbons.

After evaporation of the ether, the liquid distilled between 70° and 200°, and a bituminous residue remained in the flask. The distilled liquid was rich in hydrocarbons. We would have pursued the work, but it appeared that it contained unsaturated hydrocarbons since a solution of silver nitrate in ammoniacal potash was readily reduced to silver in the test-tube used in the experi-

ment. This reaction cannot be ascribed to an aldehyde since the liquid is not colored by fuchsine bisulphite.

Water vapor at dull redness decomposes this carbide with evolution of light, giving a black oxide and evolving carbon dioxide.

Analysis. ESTIMATION OF THE TOTAL CARBON.—The total carbon was determined either by treatment with chlorine or by direct combustion.

The figures given by the first method are a little high; the combustion of the carbon obtained after treatment with chlorine left a residue of 2 to 3 per cent. The figures obtained by this proceeding are the following:

Carbide A.	1.	2.	3.	4.
Residue after treatment with chlorine then ignition in hydrogen	12.062	13.009	11.781	10.475
Residue after combustion in oxygen	2.670	3.036	2.382	1.550
Carbon burned (by difference)	9.392	9.973	9.399	8.925

On using the second method the carbide burned easily in oxygen, giving green uranium oxide and carbon dioxide. This proceeding has the advantage of giving, in the same sample, the content of uranium and carbon.

The carbon dioxide, collected in potash and weighed, gave:

	Carbide A.		
	1.	2.	Carbide B.
Total carbon	8.67	9.02	8.38

DETERMINATION OF COMBINED CARBON AND GRAPHITE.—The combined carbon was determined by difference, by subtracting the weight of the graphite from the total carbon.

The graphite was analyzed:

(1) By treating the carbon from the chlorine treatment with boiling nitric acid and weighing on a tared filter:

	Carbide A.	Carbide C.		
Graphite	1.3	1.1	1.2	1.08

(2) The carbide was treated with boiling dilute hydrochloric acid and the graphite collected on a tared filter or on glass wool. In the latter case, it was burned and weighed as carbon dioxide:

	Carbide A.	Carbide B.
Graphite (on tared filter)	1.6	..
Graphite (by combustion)	1.58	1.6

DETERMINATION OF THE URANIUM.—The method of precipitation of uranium by ammonia gave too low figures; the best results were obtained by directly burning the carbon in oxygen and weighing the residue after ignition in a current of hydrogen.

	Carbide A.			
	1.	2.	Carbide B.	Carbide C.
Uranium	90.3	91.1	91.3	91.13

DETERMINATION OF THE NITROGEN.—The specimens of carbide, prepared in the electric furnace, always contained a small quantity of nitrogen, easily detected by means of fused potash. This nitrogen was determined volumetrically by the method of Dumas.

Nitrogen ..... 0.4 to 0.2 per cent.

Calcium.—Some samples, when heated too long, contained 0.1 to 0.2 per cent. of calcium. It is probable that it is this calcium, combined with carbon, which gave the evolution of acetylene.

Deducting the nitrogen and graphite, the following figures are obtained as combined carbon and uranium:

	A_1.	A_2.	A_3.	Theoretical.
Combined carbon	7.6	7.5	6.9	6.97
Uranium	92.4	92.5	93.1	93.02

This corresponds to the formula Ur_2C_3 for Ur = 240 and Ur_4C_3 for Ur = 120.

In another series of experiments made in a carbon tube closed at one end and through which a current of hydrogen passed, we were able to prepare a pure carbide of uranium free from nitrogen, giving, on analysis, the following figures:

	1.	2.
Combined carbon	7.20	7.16
Uranium	92.86	92.79

Uranium heated in the electric furnace, in presence of an excess of carbon, gives a definite crystalline carbide having the formula Ur_2C_3.

This compound is decomposed by cold water and gives about a third of its carbon as hydrocarbon gases rich in methane. The other part of the carbon forms a mixture of liquid and solid hydrocarbons and bituminous material. It is probable that this complex reaction resembles the phenomenon of polymerization analogous to that described by Berthelot in his work on the decomposition of hydrocarbons by heat.

The presence of hydrogen in the gaseous mixtures, on the other hand, can be due to a secondary reaction of uranium hydroxide which can be a powerful reducing agent. Péligot has shown that anhydrous uranium protoxide is greedy for oxygen, that it is pyrophoric, and that there exists a lower oxide which has the property of decomposing water.

It is seen by these experiments that the reaction of certain carbides on water can be somewhat complex. This decomposition appears more remarkable as it gives gaseous, liquid, and solid hydrocarbons, the starting-point of organic compounds, by the simple action of water at the ordinary temperature on a metallic carbide.

CLASSIFICATION OF THE CARBIDES

New Theory for the Formation of Petroleum

I will summarize in these conclusions all of my work on the metallic carbides. At the high temperature of the electric furnace, some metals, such as gold, bismuth and tin, do not dissolve carbon.

Fused copper takes up only a very small quantity, but sufficient to change its properties and modify its malleability.

Silver, at its boiling temperature, dissolves a small quantity of carbon which separates, on cooling, under the form of graphite.

This fused silver, obtained at a very high temperature, shows a very curious property; it increases in volume on passing from the liquid to solid state. This phenomenon is analogous to that known in iron.

Silver and iron contract on passing from the liquid to the solid state. On the contrary, carbon containing iron and silver under similar circumstances increases in volume.

Aluminum possesses similar properties.

The platinum metals at their boiling temperature readily dissolve carbon and separate it as graphite before solidifying. This graphite swells with acid. On the contrary, a large number of metals, at the temperature of the electric furnace, form definite crystalline compounds.

On heating a mixture of lithia or lithium carbonate with carbon in the electric furnace, I have been able to obtain lithium carbide in transparent crystals, evolving, per kilo, 587 liters of pure acetylene gas.

Similarly, by heating in my electric furnace a mixture of the oxide and carbon, I have been the first to obtain, by a general method, pure and crystalline carbides of calcium,[1] barium, and strontium in large quantities. All of these carbides are decomposed by cold water with evolution of acetylene. The reaction is complete and the gas obtained is absolutely pure. The three alkaline earth carbides correspond to the formula RC_2 and lithium carbide to the formula Li_2C_2.

[1] The carbides of calcium and barium had been previously obtained as black, amorphous, and very impure powders.

The technical preparation of acetylene is based on this reaction. Another type of carbide crystallizing in transparent hexagonal plates, 1 cm. in diameter, is furnished by aluminum. The metal, strongly heated in the electric furnace, in presence of carbon, is filled with yellow leaves of carbide, which can be separated by very careful treatment with a dilute solution of ice-cold hydrochloric acid.

This metallic carbide is decomposed by water, at the ordinary temperature, giving alumina and pure methane gas. It corresponds to the formula Al_4C_3.

Lebeau,[1] under similar conditions, obtained glucinum carbide which also gives pure methane with cold water. The cerite metals give crystalline carbides whose formulas are similar to the carbides of the alkaline earths.

We studied particularly the decomposition by water of the carbides of cerium, CeC_2, lanthanum, LaC_2, yttrium, YtC_2, and thorium, ThC_2.[2]

All of these bodies decompose water and give gaseous mixtures rich in acetylene and containing methane. With thorium carbide, the acetylene decreases and the methane increases.

The first experiments made on iron gave no crystalline compounds. By slowly cooling cast iron saturated with carbon at 3500°, the iron gave no definite compound. It is, however, possible to attain a crystalline carbide by sudden cooling. According to the work of Troost and Hautefeuille, manganese forms a carbide, Mn_3C. This carbide can be prepared in the electric furnace, and in contact with cold water, is decomposed, giving a mixture of equal volumes of methane and hydrogen.

Uranium carbide, Ur_2C_3, which I obtained, shows a more complex reaction. This carbide appears well crystallized, and in thin leaves is transparent; it is decomposed by water, giving a gaseous mixture which contains a large quantity of methane, hydrogen and ethylene. But the most interesting fact presented by this carbide is that cold water not only evolves hydrocarbon gases, but there is also a large amount of liquid and solid hydrocarbons

[1] Lebeau : "Préparation du carbure de glucinum," *Compt. rend.*, **121**, 496.

[2] Moissan and Étard : "Sur les carbures d'yttrium et de thorium," *Compt. rend.*, **122**, 73.

formed. Two-thirds of the carbon of this compound appeared in this form.

Cerium and lanthanum carbides, when decomposed by water, also gave liquid and solid hydrocarbons, but in smaller quantity.

These carbides which decompose water at the ordinary temperature, with formation of hydrocarbons, constitute the first class of the compounds of the metallic carbide family.

The second class is formed of carbides which do not decompose water at the ordinary temperature, such as the carbides of molybdenum, Mo_2C, of tungsten, W_2C, of chromium, Cr_4C and Cr_3C_2.

These compounds are crystalline, opaque and metallic-appearing. They possess great hardness and melt only at a very high temperature. We were able to prepare all of them in the electric furnace and have given the detail of the experiments as well as all of their analyses in the preceding chapters.

The metalloids with carbon at the temperature of the electric furnace give definite crystalline compounds. We mention, for example, silicon carbide, obtained in the amorphous condition by Schutzenberger,[1] and later prepared in beautiful crystals by Acheson; titanium carbide, TiC, whose hardness is so great that it scratches soft diamond; zirconium carbide, ZrC,[2] and vanadium carbide, VC.

In general, from the investigations made in the electric furnace it is seen that the compounds which are formed at a high temperature have always a very simple formula and frequently there is but one combination.

The reaction which appears most characteristic in this work is the ready formation of hydrocarbon gases, liquids, or solids by the action of cold water on some of these metallic carbides. It seems possible that these studies may present some interest to geologists. The evolution of methane more or less pure which takes place in certain regions and which lasts for centuries possibly has its origin in the action of water on aluminum carbide.

A similar reaction would explain the formation of liquid hydrocarbons. The theories for the formation of petroleum are as fol-

[1] Schutzenberger : *Compt. rend.*, **114**, 1089.

[2] Moissan and Lengfeld : "Sur un nouveau carbure de zirconium," *Compt. rend.*, **122**, 651.

lows: (1) Production by the decomposition of organic animal or vegetable matter; (2) formation of petroleum by purely chemical reactions, a theory given first by Berthelot,[1] and which has been made the subject of a paper by Mendeléeff; (3) production of petroleum by volcanic phenomena, a hypothesis given by Humboldt in 1804.

From 4 kilograms of uranium carbide, we obtained, in a single experiment, more than 100 grams of liquid hydrocarbons. The mixture thus obtained was largely formed of ethylene hydrocarbons and a small quantity of acetylene and saturated hydrocarbons. These hydrocarbons appear in presence of a large proportion of methane and hydrogen at the ordinary temperature and pressure, which leads to the thought that if the decomposition takes place at a higher temperature, there are only formed saturated hydrocarbons analogous to petroleum.

Berthelot has shown that the direct addition of hydrogen to an unsaturated hydrocarbon can be produced by heat alone. The existence of these new metallic carbides, decomposed by water, can modify the theoretical ideas which have been heretofore given to explain the formation of petroleum.

It is certain that we must guard against too hasty generalizations.

There are probably petroleums of different origins. At Autun, for example, the bituminous schists appear to have been produced by the decomposition of organic matter.

On the contrary, in Limagne the asphalt permeates all the fissures of the soft, marshy limestone, which contains very few fossils. This asphalt is in direct connection with veins of peperite (basaltic tufa) on account of the evident relation with the volcanic eruptions of the Limagne. A recent boring in Riom, 1200 meters deep, gave several liters of petroleum. The formation of this liquid hydrocarbon in this region can be attributed to the action of water on metallic carbides.

We have shown with calcium carbide under what conditions this compound can be burned and give carbon dioxide. It is probable that in the first geological periods of the earth nearly all of the

[1] Berthelot: "Sur l'origine des carbures et des combustibles minéraux," *Ann. chim. phys.*, (4), 9, 481 (1866).

carbon existed as metallic carbides. When water intervened the metallic carbides gave hydrocarbons and the latter, by oxidation, carbon dioxide. An example of this reaction can be found in the neighborhood of Saint-Nectaire. The granites, which form in this place the border of a tertiary basin, continually give off large quantities of carbon dioxide gas.

We believe also that certain volcanic phenomena can be attributed to the action of water on the easily decomposable metallic carbides. Geologists know that the last manifestation of a volcanic center consists of the emanations of various hydrocarbons becoming asphalt and petroleum and finally, as a complete oxidation product, carbon dioxide.

A movement of the crust produced by the action of water on the metallic carbides can produce a violent evolution of gases; at the time the temperature is raised, the phenomenon of polymerization of the carbides intervenes to furnish an entire series of complex products.

Hydrocarbons can then be produced at first. The phenomenon of oxidation then appears and complicates the reactions. In certain places, a volcanic fissure can act as a powerful vent. It is known that the nature of the gas collected from fumaroles varies if the volcano is submerged in the ocean or surrounded by atmospheric air. At Santorin, for example, Fouqué collected free hydrogen in the mouths of submarine volcanoes, while only water vapor is formed in aerial fissures.

These carbides exist at high temperatures and probably exist in the depths of the earth,[1] in which case their decomposition would explain the formation of solid, liquid and gaseous hydrocarbons and possibly the cause of some volcanic eruptions.

[1] The difference between the mean density of the earth and the upper crust indicates the existence of a central mass rich in metal.

SILICIDES

The method by which the definite and crystalline metallic carbides can be obtained, can be applied to the preparation of silicides. These compounds have been hitherto poorly studied and few were known. We give as example the action of silicon on iron, chromium and silver; these three metals were particularly chosen after some preliminary investigations.

A. Iron Silicide

Investigations on silicon containing cast irons are numerous, but little work exists on crystalline iron silicide. By the action of silicon chloride on iron heated to redness, Frémy obtained crystals[1] of silicide having the formula FeSi.

Hahn[2] has shown the existence of an amorphous silicide, Fe_2Si, which, when treated with hydrochloric acid, gives a crystalline residue of FeSi.

We also call attention to the thermal study of Troost and Hautefeuille on silicon containing cast irons.[3]

We have been able to obtain a crystalline iron silicide by direct union of iron and silicon, either in a reverberatory furnace heated with retort carbon or in the electric furnace.

Preparation.—(1) A layer of crystalline silicon representing about one-tenth the weight of the metal used is placed in a porcelain boat. On this silicon a cylinder of soft iron is laid and placed in a porcelain tube through which passes a slow current of pure hydrogen. It is heated by retort carbon to a temperature which causes the tube to bend, but which is below the fusion-point of wrought iron, as shown in a preliminary experiment.

After the heating, a hard, brittle, silver-white, crystalline iron silicide is formed, embedded in an excess of metal.

In this experiment where two solid elements, silicon and iron, are heated to about 1200°, and below their melting-point, a fused metallic ingot is formed. It appears that the vapor-tension of

[1] Encyclopédie chimique, Frémy, article on iron.

[2] Hahn : "Chemical Investigation of the Products of the Solutions of Cast Iron in the Acids," *Ann. Chem. Pharm.*, **124**, 57.

[3] Troost and Hautefeuille : "Étude calorimétrique des siliciures de fer et de manganèse," *Compt. rend.*, **81**, 261.

solid silicon permits this non-metal to unite with iron and give a silicide more fusible than the metal. We have already observed similar phenomena with boron, and think that the same explanation can be given for the penetration of carbon into iron at 1200°; silicon, boron and carbon have a vapor-tension which, though slight, allows the formation of solid or liquid compounds with iron, below its melting-point.

(2) Four hundred grams of wrought iron with 40 grams of crystalline silicon are placed in a crucible[1] in the electric furnace.

It is heated four minutes with a current of 900 amperes at 50 volts. The experiments should be performed quickly to avoid the formation of carbon silicide. If the proportion of silicon is increased the fusion obtained becomes difficult to attack by the acids and it is nearly impossible to separate the silicide formed.

(3) It is possible to heat a mixture of iron oxide and crystalline silicon in the electric furnace, when easily volatile silica and a fusion of iron silicide containing an excess of metal is obtained.

In an experiment made at the temperature of a good forge, we heated cylinders of wrought iron in crystals of silicon. Always under these conditions each crystal of silicon was coated with a thin layer of nitride and oxide, which retarded complete fusion and the union of the non-metal into a fused mass. After the experiment, the iron cylinders, taken from the mass, preserved their form, and were not fused in any portion. They were transformed into silicide to the center of the cylinder and it was possible to separate as silica the 2 per cent. of silicon contained. This is another example of the vapor-tension of silicon and silica below its fusion-point. The metallic fusions prepared by any of these methods are treated with nitric acid diluted with four times its volume of water. The attack, very energetic at the beginning, subsides as the metal disappears. After decantation and washing, there remains a crystalline silicide of the formula Fe_2Si.

Physical Properties.—Iron silicide appears in small, bright, prismatic crystals having a metallic appearance; its density is 7 at 22°; its melting-point is below that of iron and above that of cast iron. It acts on the magnetic needle.

[1] The carbon of the crucible does not take part in this reaction, since we have shown that in a fused cast iron, silicon can easily displace carbon.

Chemical Properties.—Hydrofluoric acid in aqueous solution attacks iron silicide, and the action is very energetic. This result does not accord with the work of Hahn, who mentions the existence of an iron silicide not attacked by hydrofluoric acid. When the silicide is reduced to a fine powder, hydrochloric acid slowly attacks it. Nitric acid is without sensible action on it, but aqua regia destroys it with formation of silica.

The gaseous halogens attack iron silicide at a temperature from dull to bright redness.

Fused potassium nitrate and chlorate are without action. The fused alkaline carbonates attack it slowly, while a mixture of nitrate and carbonate readily decompose it.

Analyses.—Iron silicide was heated with a mixture of alkaline nitrate and carbonate; the iron was weighed as sesquioxide and the silicon as silica. We obtained the following figures:

	1.	2.	3.	4.	Theoretical.
Iron.....	79.20	81.10	82.12	81.43	80.00
Silicon ...	20.95	19.04	18.02	18.59	20.00

Since our first work, Lebeau[1] has obtained an iron silicide of the formula FeSi by taking advantage of the property which this body possesses of dissolving in fused copper silicide, and crystallizing on cooling.

A mixture of 400 grams of copper silicide and 40 grams of pure iron filings is placed in a carbon crucible and heated in the electric furnace with a current of 950 amperes at 45 volts. A homogeneous fusion is obtained, which is crystalline and has a white metallic fracture like copper silicide. The product treated with dilute nitric acid, then washed with soda to remove the silica formed, leaves bright crystals which have a metallic appearance. This is iron silicide, FeSi, obtained by Frémy and Hahn.

Lebeau showed that this method can be applied to the preparation of other silicides as those of cobalt, nickel and chromium.

B. Chromium Silicide

(1) When fused chromium containing 2 per cent. of carbon (a metal more infusible than iron) is introduced into a boat lined

[1] "Sur un nouveau procédè de prèparation du siliciure de fer SiFe." *Compt. rend.*, 128 933.

with silicon and heated to 1200° in hydrogen, it is possible to obtain a fusion of chromium silicide.

Silicon, here also, on account of its vapor-tension in the solid state, passes into the chromium, causing fusion.

To succeed with this experiment, it is necessary to carefully construct the reverberatory furnace and increase the draught by a pipe 10 or 12 meters long. In some of the experiments, the porcelain tube is flattened and the two sides become fused together.

(2) Carbon, free from chromium, is heated with 15 per cent. of its weight of silicon in a carbon crucible. Using a current of 900 amperes at 50 volts, the heat should last nine minutes.

A fused mass with a metallic fracture is obtained, which contains the silicide embedded in an excess of metal.

(3) A mixture of 60 parts silica, 200 parts of chromium sesquioxide and 70 parts of sugar carbon was heated for ten minutes in the electric furnace with a current of 950 amperes at 70 volts. A well-fused mass which was brittle and distinctly crystalline was obtained. Some geodes found in the interior of the metal were covered with needles of chromium silicide.

The coarsely powdered metallic fusions were treated with cold concentrated hydrofluoric acid in the cold. After a few moments the action is energetic, but can be moderated by adding a little water to avoid the elevation of temperature which would cause the silicide to be attacked. It is washed with water and again treated with concentrated hydrofluoric acid in the cold until the action ceases. The silicide, Cr_2Si, is finally obtained in small prisms either single or united. This silicide is often contaminated with a small quantity of crystalline carbon silicide which we have not been able to separate and make a complete analysis.

The chemical properties resemble those of iron silicide. It acts like it with the acids. Chlorine attacks it at redness with evolution of light. Gaseous hydrochloric acid, about 700° transforms it into silicon chloride and chromium chloride. Fused potassium nitrate gives a chromate and silicate, while fused potash attacks it slowly. Chromium silicide scratches quartz and corundum with great ease. Most of the silicides possess a much greater hardness than the corresponding silicides. Among these compounds harder bodies than carbon silicide are found.

Analysis.—The analyses of chromium silicide presented some difficulties. It was attacked by a mixture of 2 parts potassium carbonate and 8 parts potassium nitrate, and the fusion dissolved in hydrochloric acid. The separation of the silica which is rendered insoluble in acids by two successive treatments on the sand-bath is always delicate. The presence of carbon silicide which is separated by a special treatment with acids and the existence of chromium carbosilicide in some specimens makes the analysis complicated. We obtained the following results:

	1.	2.	3.	Theoretical for Cr_2Si.
Chromium.....	80.22	79 83	80.36	78.79
Silicon	19.60	21.08	19.92	21.21

C. Manganese Silicide

About 1857 Brunner[1] observed that the manganese obtained by reducing the chloride or fluoride with sodium in a porcelain boat showed different properties than that obtained by reduction of the oxide with carbon. A little later Wöhler[2] observed that this manganese when treated with hydrochloric acid gave silica; a number of analyses showed a content of from 0.6 to 13.37 per cent. of silicon.

Troost and Hautefeuille,[3] in a work on the heat evolved in certain combinations, have showed that silicides of 8.2 to 12 per cent. silicon contained more than 1 per cent. carbon.

Vigouroux[4] obtained a crystalline manganese silicide, having the formula Mn_2Si, in three different ways, by heating in the electric furnace: (1) A mixture of silicon with the metal; (2) a mixture of silicon and oxide; (3) a mixture of carbon, silica and the oxide.

Properties.—Mn_2Si is hard, brittle and crystalline. Its density is 6.6; it is not altered in the air. Fluorine attacks it at the ordinary temperature, chlorine about 500°, while bromine and iodine act with more difficulty. Oxygen gives the oxide at redness. It is easily attacked by the halogens. Fused potash, and a mixture

[1] Poggendorff: *Annalen*, **101**, 264.

[2] Wöhler: *Ann. Chem. Pharm.*, **106**, 1858.

[3] Troost and Hautefeuille: "Étude calorimetrique sur les carbures, siliciures, borures de fer et de manganese," *Ann. chim. phys.* (5), p. 9 (1876).

[4] Vigouroux: *Compt. rend.*, **121**, 771.

of alkaline nitrate and carbonate easily attacks it. These reactions can be used for the analysis.

D. Silicides of Nickel and Cobalt

These silicides have been obtained by Vigouroux[1] by heating 10 parts by weight of silicon with 90 parts of metal, in a carbon crucible in the electric furnace. Combination first takes place, then the excess of metal distils and the purer silicide remains. The fusion obtained is gray-white, very hard and brittle. It is treated with nitric acid to remove the excess of metal, when a silicide remains which corresponds to the formula Ni_2Si or Co_2Si.

Properties.—The silicides of nickel and cobalt are crystalline bodies of a steel-gray color. They fuse more easily than silicon or the metal and stand very high temperatures without decomposing. They burn in fluorine and chlorine with evolution of light. Bromine and iodine act with more difficulty. Dry hydrochloric acid gas slowly attacks them at redness. The action is similar with dry hydrobromic and hydriodic acid gases. Hydrofluoric acid attacks them readily while the other acids act very slowly.

Analysis.—The finely powdered silicide is treated with aqua regia, evaporated to dryness, and taken up in hydrochloric acid when the metal goes into solution.

		1.	2.	Theoretical for Ni_2Si.
Silicide of nickel	Si	18.36	19.25	19.28
	Ni	81.66	81.00	80.72

		1.	2.	Theoretical for Co_2Si.
Silicide of cobalt	Si	20.04	19.12	19.25
	Co	80.70	80.28	80.75

E. Copper Silicide

Berzelius[2] knew that copper, when strongly heated in the blowpipe with silicon and treated with acid, left a skeleton of silica. Deville and Caron[3] mention alloys containing these two elements which they called "aciers de cuivre" whose silicon content was as high as 12 per cent.

Vigouroux[4] has been able to obtain a series of alloys by heating

[1] Vigouroux : " Sur les siliciures de nickel et de cobalt," *Compt. rend.*, **121**, 686.
[2] Berzelius : *Ann. chim. phys.* (2), p. 27 (1824).
[3] Sainte Claire-Deville and Caron : *Compt. rend.*, **45**, 1863.
[4] Vigouroux : *Compt. rend.*, **122**, 318.

a mixture of silicon and pure copper in the electric furnace. By volatilizing the excess of copper by heat, a fusion remains which, when slowly cooled, contains geodes of crystals which have the formula Cu_2Si.

Properties—Copper silicide, Cu_2Si, is a very hard and brittle substance with a steel-gray color and a density of 6.9. It dissolves large quantities of silicon which it deposits in leaves. Oxygen acts on it at a red heat , but it alters in the cold in moist air. The halogens attack it readily as do the halogen acid gases. The fused alkaline carbonates attack it completely if it is finely powdered. These reactions have been used in its analysis.

ACTION OF SILICON ON SILVER

When a mixture of crystalline silicon and pure silver is heated in the electric furnace, if the temperature is very high, a metallic fusion is obtained which is covered with beautiful crystals. At first sight they could be taken for silver silicide, but, on dissolving the silver in nitric acid, a residue of transparent, yellow, hexagonal crystals is obtained, the analysis of which shows they are formed of carbon silicide.

When the temperature of the electric furnace is lower, the silicon separates from the silver before solidification; it partly separates into crystals, which are transparent under the microscope, and similar to those described by Vigouroux.[1]

The silver which surrounds these crystals, on analysis, shows no trace of silicon. The same experiment was made in a reverberatory furnace, but the silver retained no silicon. This was also true in the experiments which were made in the forge or in the Pérrot furnace, in which the silicon produced by the method of Deville (action of sodium on fluosilicate) came in contact with melted silver. In these experiments liquid silver dissolved the silicon, but separated it in the crystalline state at the moment of solidification. This phenomenon is similar to the action of phosphorus on silver. This metal dissolves considerable phosphorus above 1000° and at the exact point when it passes from the solid to the liquid state, the vapor of the phosphorus is given off, as is the case with oxygen.[2]

[1] Vigouroux : "Sur la rèduction de la silice par aluminium," *Compt. rend.*, **120**, 1161.

[2] Hautefeuille and Perrey : "Sur le rochage de l'or et de l'argent dans la vapeur de phosphore," *Compt. rend.*, **98**, 1378.

Conclusions.—The action of silicon on the metals can give three different results:

(1) Solid silicon, due to its vapor-tension, can unite with a solid metal and give by an action similar to cementation, a true silicide, whose melting-point is less than that of the metal.

(2) Liquid silicon can unite with the fused metals in the electric furnace.

(3) Silicon is dissolved in fluid metals, not forming a combination with them or a very unstable one, and separating as crystalline silicon at the moment of solidification.

Vigouroux in a study on amorphous silicon and its compounds has pursued the study of the preparation of silicides in the electric furnace. He obtained crystalline silicides of nickel, cobalt, manganese, copper and platinum.

F. Platinum Silicide

Boussingault[1] and Winckle[2] obtained alloys of platinum containing varying quantities of silicon. By heating the metal and silicon in the furnace for tubes, Vigouroux[3] obtained a white, very hard and very brittle alloy which had a density of 13.8 and corresponding to the formula Pt_2Si.

The analysis was made by treating with aqua regia and evaporating to dryness to render the silica insoluble. The following figures were obtained:

	1.	2.	Theoretical for Pt_2Si.
Silica	6.92	6.95	6.68
Platinum	93.08	93.40	93.32

G. Carbon Silicide[4]

Amorphous carbon silicide, SiC, was discovered by Schutzenberger.[5] Acheson has obtained crystalline carbon silicide colored blue by iron by heating a mixture of silica, coke, alumina and sodium chloride in the electric furnace. He began the technical preparation of this compound on account of its great hardness and named it carborundum.

[1] Boussingault: *Ann. chim. phys.*, 2e série, **16**, and 5e série, **8**, 1821 and 1876.
[2] Winckle, Pelouzè, and Frèmy: *Traité de chimie*, Vol. III, p. 1267.
[3] Vigouroux: *Compt. rend.*, **123**, 115.
[4] H. Moissan: *Compt. rend.*, **117**, 425, September 25, 1893.
[5] Schutzenberger: *Compt. rend.*, **114**, 1089 (1892).

In the studies which I made on the crystallization of carbon, I found in ingots of silicon, fused in the wind-furnace in a layer of carbon, small crystals of carbon silicide, but I did not publish anything at this time on the subject so the discovery of crystalline carbon silicide belongs to Acheson. The study of the action of the electric arc on silicon led to the preparation of the crystalline silicide by four different methods.

(1) *Direct Combination of Silicon with Carbon.*—By attempting to dissolve carbon in silicon kept in a fused condition in a wind-furnace, we obtained this compound as beautiful crystals several millimeters long; these crystals were got out by dissolving the fusion of silicon in a boiling mixture of concentrated nitric acid and hydrofluoric acid. This first preparation showed that carbon silicide is readily formed by means of a solvent, at a temperature between 1200° and 1400°.

(2) *Preparation in the Electric Furnace.*—The same compound is prepared more simply by heating, in the electric furnace, a mixture of silicon and carbon, in the proportions of 12 parts of carbon and 28 of silicon. Under these conditions there is obtained a mass of crystals which are purified very easily by first introducing into a boiling mixture of hydrofluoric and concentrated nitric acids, then by treatment with the oxidizing mixture of Berthelot—nitric acid and potassium chlorate. The crystals are frequently colored yellow, but can be obtained completely transparent, while again they sometimes show a sapphire-blue color. The transparent crystals are made by working rapidly in a closed carbon crucible and using silicon as free as possible from iron.

Crystallization in Fused Iron.—Iron silicide is heated in the electric furnace in presence of an excess of silicon. The resulting fusion is treated with aqua regia to remove the iron. The crystalline residue is kept several hours in a mixture of concentrated nitric acid and hydrofluoric acid and, finally, treated eight or ten times with an oxidizing mixture of potassium chlorate and nitric acid.

A metallic fusion containing crystals of carbon silicide is prepared in a similar manner by heating a mixture of iron, silicon.

and carbon in the electric furnace, or simpler, a mixture of iron, silica and carbon.

(3) *Reduction of Silica by Carbon.*—It is possible to obtain the same compound by reducing silica with carbon in a crucible in the electric furnace. The crystals of carbon silicide, thus prepared, are less colored than those obtained by solution in iron, when pure silica and iron are used.

(4) *Action of the Vapor of Carbon on the Vapor of Silicon.*—A more original proceeding for the preparation of carbon silicide consists in making the vapor of carbon act on the vapor of silicon. The experiment was made in a small carbon crucible of elongated shape containing fused silicon. The bottom of the crucible is heated to the highest temperature of the electric furnace. After the experiment, slightly colored, very hard and brittle crystals in prismatic needles of carbon silicide are found.

Properties.—Crystalline carbon silicide is a body which is formed at a high temperature. It is very stable and resists the most energetic agents. Schutzenberger has shown this property for the amorphous silicide.

Carbon silicide, free from iron, is colorless; the well-formed crystals sometimes show regular hexagons (Fig. 42).

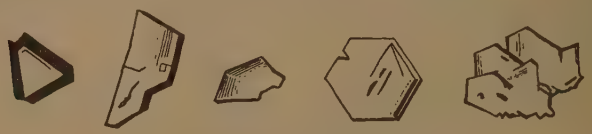

Fig. 42. Silicide of carbon magnified 10 diameters.

Some show, rarely, however, triangular impressions and parallel striations; at first sight, to the trained eye, it is impossible to mistake them for the diamond. Moreover, these crystals act strongly on polarized light and show strong colors. Their density is 3.2; they possess great hardness, easily scratching chrome steel and the ruby. It is only necessary to rub, with a hard wood point, some powder of crystalline carbon silicide on a polished surface of a ruby to obtain a very deep scratch.

Heated in oxygen at 1000°, it is unchanged. It can be ignited in air with a Schloesing blowpipe without showing a trace of combustion. Sulphur vapor does not attack it at 1000°. In a

current of chlorine at 600° for an hour and a half, it is attacked only on the surface.[1] The action becomes complete at 1200°. Fused potassium nitrate and chlorate are without action. The same is true with boiling sulphuric and hydrofluoric acid. The mixture of concentrated nitric acid and hydrofluoric acid, which readily dissolves silicon, is without action on carbon silicide. Lead chromate attacks the compound, but in order to burn it completely in a glass tube, it must be treated a number of times.

Fused caustic potash decomposes the silicide; it first causes a cleavage, and finally dissolves it after heating an hour to dull redness with formation of potassium carbonate and silicate. This latter reaction permits the estimation of the silica, while the carbon can be weighed as carbon dioxide, by combustion with lead chromate.

Analysis.—The determination of carbon was made on 0.100 gram to 0.200 gram which was heated in a platinum boat with lead chromate to a temperature a little above 1000°. The experiment was carried out in a tube of Berlin porcelain through which a current of oxygen passed.

The silicon weighed as silica was obtained by treating 0.200 gram of silicide with a mixture of fused potassium nitrate and carbonate; the residue was taken up with hydrochloric acid, then evaporated to dryness. The analysis was then made as usual in the determination of silica in a silicate. We obtained the following figures:

	1.	2.	Theoretical.
Silicon	69.70	69.85	70.00
Carbon	30.00	29.80	30.00

These analyses show that the crystals of carbon silicide prepared by the different methods described, always correspond to the formula SiC. At the temperature of the electric arc there is only one combination of silicon and carbon, the simplest consisting of 1 molecule of each element. This silicide, whose stability is great, can serve as a type of the new compounds prepared by means of the electric furnace.

[1] 0.283 gram lost only 0.012 gram.

BORIDES

Like silicon and carbon, boron can give a series of compounds equally definite and crystalline. The study of these new series enriches chemistry with very stable bodies, certain of which will likely have technical applications. Moreover, they give useful indications for the establishment of valence and classifications of the elements.

A. Borides of the Alkaline Earths[1]

Preparation of Calcium Boride.—We heated in the electric furnace, in a tube closed at one end, an intimate mixture of 10 grams of pure boron and 50 grams of quicklime. The experiment lasted seven minutes with a current of 900 amperes at 45 volts. On cooling, there remained in the tube a fused mass which was brittle, somewhat hard and with no crystalline appearance. This substance was slowly attaked by water and almost completely soluble in hydrochloric acid, leaving a slight residue. The latter, examined under the microscope, showed graphite, rectangular and cubic crystals, yellow crystals in thin leaves, and very small dark-colored ones. The crystalline portion, which was not attacked by hydrochloric acid, was rapidly destroyed by nitric acid and contained only calcium and boron.

The yield was very small so we modified the reaction. A mixture of 10 grams calcium carbide and 1 gram pure boron was heated in the electric furnace. The boron did not appear to displace the carbon of the calcium carbide; there was formed, however, a small quantity of calcium boride, but the formation appeared to be due more to dissociation than to the direct action of boron on the carbide. This was also the case in the action of sugar carbon on calcium borate or in the action of calcium carbide on the borate of the same metal, at the temperature of the electric furnace. To increase the yield, it was necessary to produce the boron in the mixture and this was done in the following manner:

A mixture was made of 1000 grams pure, dry calcium borate, 630 grams of pure aluminum shavings and 200 grams finely pulverized sugar carbon. These substances were carefully dried and

[1] This work was done with Williams.

the calcium borate was intimately mixed with the carbon, and the aluminum added. This mixture was heated for seven minutes in a carbon crucible in the electric furnace, with a current of 900 amperes at 45 volts. The quantity of aluminum was made sufficient to completely reduce the calcium borate. The carbon was added to prevent the formation of alumina, which is difficult to separate from the calcium boride. A part of the aluminum appears after the experiment as carbide which is readily decomposed by water and dilute hydrochloric acid.

The length and regularity of the heating are of great importance as to yield of calcium boride. The fusions, which were obtained on cooling the mass, were homogeneous and showed a crystalline metallic fracture. They were broken into pieces and treated with dilute hydrochloric acid until action ceased. During this operation, a large quantity of gas was evolved which had a very disagreeable odor and which contained hydrogen, acetylene, methane and hydrogen boride. The residue was treated with boiling concentrated hydrochloric acid and washed with water. The substance which remained after these treatments consisted largely of crystals of calcium boride and a small quantity of organic matter which was lighter than that given by the action of hydrochloric acid on the original fusion.

On account of its lightness, it was possible to remove this organic matter by washing with water. The residue was then washed with ether and with toluene. These liquids took on a deep coloration and removed a fresh quantity of organic matter which it was possible to collect by evaporating the solvent. A brown, resinous substance was obtained which could be readily nitrated with fuming nitric acid, giving a yellow-colored body which was soluble in ether. After repeated washing with toluene and ether, the calcium boride was treated with cold hydrofluoric acid, washed with cold water and after drying extracted with ether until the latter no longer showed a coloration. The crystalline powder obtained was washed again with water, then with alcohol and finally dried *in vacuo*.

The crystalline powder was not absolutely pure; it still contained a small quantity of graphite and a little carbon boride.

Physical Properties.—Calcium boride appears as a bright, black, crystalline powder. Examined under the microscope it shows small, rectangular or cubic crystals, which in thin section are transparent and of a yellowish color. The compound easily scratches quartz and is hard enough to scratch the ruby. Its density at 15° is 2.33. Heated in the electric furnace, it fuses to a homogeneous mass which has a crystalline cleavage.

Chemical Properties.—Calcium boride, heated to redness in a current of dry hydrogen, is not altered. Fluorine attacks the compound in the cold with evolution of light. Chlorine attacks it at redness, evolving a large amount of heat and forming calcium chloride and boron chloride. At the same temperature, bromine and chlorine attack it, but more slowly. Heated in the air, it does not burn at bright redness. Sulphur vapor scarcely reacts at the same temperature.

Calcium boride is not decomposed at 1000° in a current of nitrogen. The boride is without action on water at the ordinary temperature. It is thus different from calcium carbide. It is without action on water even when heated to 250° under pressure. When heated above this temperature in a current of water vapor, the action is very slow. The layer of lime and boric acid which is formed prevents the decomposition from becoming rapid. At the temperature of the softening of glass, hydrogen is slowly evolved, and in order to obtain a greater quantity of gas, it is necessary to heat it to 1000°.

We have previously stated that calcium boride can be fused in the electric furnace, and would add that the fused mass is attacked by water with the evolution of hydrogen, but without formation of acetylene. This seems to indicate the presence of another boride of calcium which contains less boron and is decomposed by water. The halogen acid gases slowly attack calcium boride at dull redness. At the temperature of the softening of glass, ammonia gas is without action. Solutions of the halogen acids do not decompose calcium boride. Dilute sulphuric acid is without action, while concentrated gives sulphuric acid. Nitric acid, either dilute or concentrated, energetically attacks calcium boride.

Oxidizing agents, such as lead oxide or potassium nitrate, attack

it with violence at a red heat. Bromine water or a mixture of potassium chlorate and hydrochloric acid slowly dissolves it. On the contrary, fused potassium carbonate, bisulphate, and hydrate act energetically at redness.

Analysis.—Calcium boride was treated with nitric acid in an apparatus used for the estimation of boron.

The analysis was made by the Gooch[1] method. After driving over the boric acid with methyl alcohol, the calcium was determined in the residue by precipitating as oxalate and weighing as oxide. To determine the small quantity of carbon which the compound contained as impurity, the substance was treated with pure chlorine, the residue washed to remove the calcium chloride, thrown on an asbestos filter, then burned in oxygen and the carbon dioxide collected in weighed potash tubes. The residue, insoluble in nitric acid, was washed, dried at 110° and weighed. It was composed of small crystals of carbon boride, CB_6, which were not soluble. We obtained the following figures:

	1.	2.
Calcium	36.22	36.03
Boron	57.43	57.30
Carbon	2.66	2.82
Insoluble	1.21	1.02

By referring the figures of carbon and boron to 100 per cent. 38.66 and 38.61 per cent. calcium, and 61.33 and 61.39 per cent. boron are obtained, differing but slightly from 37.86 per cent. calcium and 62.14 per cent. boron, calculated from CaB_6.

B. Strontium Boride

Strontium boride was prepared in a similar manner to calcium boride, using a mixture of strontium borate, aluminum and carbon. This compound can be obtained very pure on account of its high density. By means of bromoform, most of the impurities which accompany strontium boride can be removed.

Physical Properties.—Strontium boride appears as a black powder consisting of small crystals. When examined under the microscope, the crystals are transparent if sufficiently thin and have a red-brown color. The crystals were larger than those of calcium

[1] Gooch: "Estimation of Boric Acid," *Am. J. Sci.*, 9, 23.

boride; they also readily scratch quartz. Their density at 15° is 3.28.

Chemical Properties.—The chemical properties of this compound are similar to those of calcium carbide, only it does not take fire in fluorine in the cold, but must be slightly heated to bring about this action.

Analysis.—The method of analysis was the same as for calcium boride. We obtained the following figures:

	1.	2.
Strontium	56.33	56.56
Boron	43.38	43.00
Carbon	0.67	0.63
Insoluble	trace	trace

The formula SrB_6 requires: Sr, 57.10; B, 42.90.

C. Barium Boride

The method previously described can be used to prepare the corresponding barium compound. It is prepared more easily than the other two. The yields are greater and the purification was easier on account of its high density.

Properties.—Barium boride has the same appearance as the other two alkaline earth borides; the crystals, although small, are very regular. Its density at 15° is 4.36, and its chemical properties are similar to those of calcium and strontium borides. Its hardness is also great, it scratches quartz and ruby, but not the diamond.

Analysis:

	1.	2.	Theoretical for BaB_6.
Barium	67.20	67.09	67.57
Boron	32.25	32.28	32.43
Carbon	0.29	0.31	...
Insoluble	trace	trace	....

D. Iron Boride

We studied the preparation of iron boride which can serve as a type for the preparation of a number of metallic borides. This preparation also shows the action of boron on the carbides of iron and has enabled[1] us with Charpy to study the action of boron on steel.

[1] Moissan and G. Charpy: "Sur les aciers au bore," *Compt. rend.*, **120**, 130.

Preparation of Iron Boride.—This compound can be obtained: (1) By the action of boron chloride on reduced iron; (2) by direct action of boron on iron.

(1) *Action of Boron Chloride on Reduced Iron.*—Pure reduced iron was placed in a porcelain tube through which a slow current of boron chloride passed. The apparatus was heated to dull redness; volatile chloride of iron was immediately formed, and in the tube there remained an amorphous boride of iron which had a gray color.

(2) *Action of Boron on Iron.*—This experiment can be made in a furnace with a tube, heated by a good coke fire. A porcelain boat is lined with the necessary quantity of boron for combination and in it is placed Swedish or reduced iron. A very slow current of hydrogen is passed through the apparatus, and the tube is heated between 1100° and 1200°. On allowing it to cool in hydrogen, a metallic fusion is obtained which, when the content of boron is about 9 per cent., shows a good crystalline texture and breaks easily along well-determined planes of cleavage. Long needles traverse the mass and frequently show iridescent colors.

When a cylinder of soft iron is brought on to pure amorphous boron, under the conditions mentioned, the boron produces a phenomenon of cementation, below the melting-point of iron which should not be reached. This fused boride, which contains 8 to 9 per cent. of boron, melts a little below that of ordinary cast iron. With the electric pyrometer of Le Chatelier we found its melting-point to be about 1050°.

If the content of boron reaches 15 per cent. the fusion becomes much more difficult, the mass shows a conchoidal fracture and the crystallization is confused. In a good coke fire or in a furnace heated with retort carbon, a mixture containing 29 per cent. of boron can be fused only with difficulty; it is better to use the electric furnace.

A fused boride can also be obtained in the electric furnace by heating, in a carbon crucible lined with boron, pieces of good wrought iron. The reaction can then be made with larger masses and with a current of 300 amperes at 65 volts the heating should not last more than five or six minutes. If the temperature is too

high, the carbon of the crucible enters into the reaction, and the fused boride contains a variable quantity of crystalline carbon boride.

The metallic fusions prepared either in the furnace with a tube or in the electric furnace were broken and treated with hydrochloric acid diluted with two or three times its volume of water. The excess of iron dissolves and there remained a crystalline substance which was washed with water, then with alcohol and ether, to avoid the action of carbon dioxide and moisture in drying. The crystals, obtained under these conditions, have a constant composition. They are iron boride having the formula FeB.

Properties.—Iron boride appears in bright crystals, of yellow-gray color, several millimeters long. Its density is 7.15 at 18°. The crystals do not alter in air or in dry oxygen. In moist air they soon become covered with a yellow layer.[1]

Heated in a current of chlorine to redness, it is attacked with evolution of light; the chlorine unites with the boron and the iron. Bromine attacks the compound with greater ease and appears to form a double bromide of boron and iron. Iodine is without action at 1100°. The same is true for hydriodic acid.

Iron boride, heated in oxygen, burns brightly and when the combustion commences at a point, it proceeds through the whole mass without the application of further heat. In all of these experiments the amorphous boride of iron is more easily attacked than the crystalline boride. Since this action of oxygen is increased when the powdered boride is in contact with moisture and carbon dioxide, it is to the existence of this iron boride that the phenomenon of evolution of light which is sometimes produced in the drying of impure boron, prepared by the action of sodium on boric acid, can be attributed. The amorphous boride is attacked by sulphur at a temperature a little above its melting-point. The crystalline boride is attacked with evolution of light, but at a higher temperature.

[1] On working over mercury, in presence of a small quantity of water and a measured quantity of air, a notable diminution of the oxygen was observed after forty-eight hours and each particle of boride was observed to be covered with a gelatinous layer having the appearance of rust.

Phosphorus at redness gives a mixture of iron phosphide and boron phosphide. Potasium chlorate at its melting-point does not attack iron boride, but when the temperature is increased, action commences and continues with evolution of light. The same is true with potassium nitrate. The fused alkaline carbonates rapidly destroy iron boride and the action is complete in a short time.

Fused potash attacks iron boride energetically, but without evolution of light. Concentrated or diluted sulphuric acid is without action in the cold. The concentrated acid at its boiling temperature decomposes iron boride with formation of sulphurous acid and anhydrous iron sulphate. Concentrated hydrochloric acid attacks this compound slowly in the cold while the dilute acid is without action and permits, as we have shown, the separation of it from the excess of metal. Aqueous hydrofluoric acid, either cold or hot, only slowly attacks this compound.

The real solvent for iron boride is nitric acid and, of course, aqua regia. Very dilute nitric acid dissolves it only when heated while fuming or concentrated acid attacks it violently.

Analysis.—The iron was always determined as oxide, titration with permanganate cannot be used with this compound. The determination of the boron was made as calcium borate, by the method of Gooch, separating the boric acid by means of methyl alcohol. In this analysis iron boride was treated with nitric acid in a special apparatus which we used for the determination, an apparatus which we have previously described.[1] After all evolution of gases had ceased, the boric acid was driven out with methyl alcohol and the liquid digested with quicklime. From the increase of weight of the lime the content of boron was obtained (see p. 290). We obtain the following figures:

	1.	2.	3.	Theoretical for FeB.
Iron	84.15	84.48	83.86	83.58
Boron	15.18	14.94	16.19	16.42

The slight excess of iron, shown in the analyses, can be explained by the fact that the crystals of iron boride always retain a little enclosed metal. The amorphous boride obtained by the

[1] *Compt. rend.*, **116**, 1087.

action of boron chloride on reduced iron gives more exact figures (analysis No. 3).

These analyses lead, for the crystalline compound which we have described, to the formula FeB. By raising the temperature of the electric furnace at the time when the boride is formed, we were unable to obtain other combinations. At the high temperatures, chemistry seems to be simpler and a single combination, having always a very simple formula, is obtained.

E. Nickel and Cobalt Borides

The borides of nickel, NiB, and cobalt, CoB, can be obtained pure and crystalline by the method used to prepare iron boride; the reaction takes place by direct action of boron on the metal. They can be prepared either in the electric furnace or in an ordinary reverberatory furnace heated with retort carbon.

Preparation in the Electric Furnace.—The metal is introduced into a carbon crucible lined with powdered boron, and heated five minutes with a current of 300 amperes at 50 volts.

Preparation in the Reverberatory Furnace.—A porcelain boat is lined with 10 to 12 grams of powdered boron. One hundred grams of metal are placed on the boron and heated in a porcelain tube through which passes a very slow current of pure, dry hydrogen. Whatever mode of heating is employed, a brittle, metallic fusion of crystalline boride with excess of metal is obtained. When the electric furnace is used, the crystallization is less perfect.

The metallic fusions are broken and treated with nitric acid diluted with an equal volume of water. With cobalt, commercial concentrated acid can be used. When the action is complete, a crystalline boride frequently remains in fusions which have the same appearance as the corresponding iron compound. The boride is washed with distilled water, then with alcohol and ether, and finally dried rapidly in the oven, since these compounds are very readily acted on by moist air.

Physical Properties.—Nickel and cobalt borides appear in bright prisms several millimeters long. The density of cobalt boride at 18° is 7.24, while that of nickel boride is 7.39. These two compounds scratch glass with difficulty; they are magnetic.

Chemical Properties.—Chlorine attacks the two borides below dull redness with evolution of light, giving boron chloride and following the precautions already given. The nickel and cobalt, With bromine, the action takes place at redness, but is not energetic. Boron bromide distils and a green residue remains in case of cobalt and yellow with nickel. The borides of nickel and cobalt, prepared in the electric furnace, are scarcely attacked by iodine at the point of softening of glass. On the contrary, the same compounds, prepared in the reverberatory furnace, are attacked under similar conditions.

At the ordinary temperature, these borides are not decomposed by oxygen or dry air, but rapidly alter in contact with moist air and particularly in presence of carbon dioxide. Below dull redness these borides burn brightly in pure oxygen. They are attacked by the vapor of sulphur about 700° with evolution of light. At its melting-point, potassium chlorate is without action, but if the temperature is raised, it attacks these borides with great evolution of heat. Fused potassium nitrate acts in a similar manner, but with less violence and without evolution of light. A mixture of sodium nitrate and carbonate gives complete transformation into black oxide and alkaline borate. The fused alkaline carbonates and the alkalies dissolve these borides without evolution of light. Under the action of water vapor at dull redness, the nickel and cobalt borides are decomposed, giving oxide and boric acid which pass off in the excess of the water vapor.

Hydrochloric acid, especially dilute, has little action on these borides. On the contrary, nitric acid acts energetically and the action of a mixture of hydrochloric and nitric acids is very violent. Dilute sulphuric acid is without action, while hot concentrated acid evolves sulphurous acid.

Analysis.—(1) The boride was treated with dilute nitric acid in an apparatus for the determination of boron. The boric acid volatilized with methyl alcohol was weighed as calcium borate, following the precautions already given. The nickel and cobalt, dissolved in nitric acid, were precipitated as oxide, washed by decantation with boiling water and subsequently weighed in the metallic state after reduction by hydrogen.

(2) The boride was attacked by a mixture of potassium nitrate and carbonate. It was taken up in water; the cobalt or nickel remained insoluble as oxide and was weighed as metal. The potassium borate was introduced into the apparatus for the determination of boron, nitric acid added, and the analysis made as we have shown.

We obtained the following figures, using 58.6 for the atomic weight of Ni and 58.7 for Co:

	1.	2.	3.	Theoretical for NiB.
Nickel	85.45	85.11	84.12	84.19
Boron	14.51	14.88	14.43	15.81

	1.	2.	3.	4.	Theoretical for CoB.
Cobalt	83.68	84.06	83.85	85.37	84.22
Boron	15.89	16.04	....	....	15.78

Conclusions.—The borides of nickel, NiB, and cobalt, CoB, are readily obtained crystalline at 1200°. These compounds have properties similar to those of iron boride, previously described. These borides enable boron to be introduced into such a metal as iron, since as we have shown[1] boron and silicon, at a high temperature, can displace carbon in a fused cast iron.

F. Carbon Boride

In the action of the electric arc[2] on boron, silicon, and carbon, we called attention to the existence of new crystalline compounds produced at a very high temperature, possessing such stability that they are not attacked by most of our reagents, and having a great hardness, sometimes as great or greater than that of the diamond. We have given a number of methods for the preparation of carbon silicide,[3] and will now describe a new similar compound, carbon boride.

Wöhler and Deville[4] in 1857 showed the existence of a variety of boron to which was given the name adamantine. Hampe,[5] re-

[1] H. Moissan: "Déplacement du carbone par le bore et le silicium dans la fonte en fusion," *Compt. rend.*, **119**, 1172.

[2] H. Moissan: "Action de l'arc électrique sur le diamant, le bore amorphe et le silicium cristallisé," *Compt. rend.*, **117**, 423.

[3] H. Moissan: "Préparation et propriétés du siliciure de carbone cristallisé," *Compt. rend.*, **117**, 425.

[4] Wöhler and Sainte-Claire-Deville: "Annales de chimie et de physique," 3e série, **52**, 63 (1858).

[5] Hampe: *Ann. Chem.* (Liebig), **183**, 75 (1876).

peating the work, has shown that it is obtained in presence of a mixture of different compounds containing particularly an aluminum boride and an aluminum borocarbide in pure and crystalline condition.

In the more recent work on the same line Joly[1] isolated in this mixture a carbon boride in which the content of carbon, after treatment with chlorine, led to the formula B_6C.

When boron acts on carbon at the temperature of the electric furnace two carbides are formed, the one stable, the other attacked by a mixture of potassium chlorate and nitric acid. The first corresponds to the formula B_6C; it is this compound that we will describe.

Formation.—This carbon boride can be produced:

(1) When the electric arc is made to play between carbons bound together with a mixture of boric acid and aluminum silicate. Under these conditions it is always contaminated with carbon silicide.

(2) When a small quantity of boron is placed in an electric arc playing between two carbon electrodes.

(3) By heating in the electric furnace to about 3000° pure boron in a small, covered carbon crucible.

(4) This boride is also formed in fused metals. It is formed by heating, in a carbon crucible in the electric furnace, an iron boride rich in boron; the fusion is treated with hydrochloric acid, then with aqua regia, and a black residue of graphite and carbon boride separates.

If a silicious cast iron is used in this experiment, the residue obtained after treatment with the acids, consists of a mixture of carbon boride and carbon silicide.

(5) By submitting to the solvent action of silver and copper in the electric furnace, a mixture of sugar carbon and pure boron, good crystals of carbon boride are obtained.

(1) *Preparation by Direct Union of Boron and Carbon.*—A mixture of 66 parts of amorphous boron and 12 parts of sugar carbon are heated in a carbon crucible in the electric furnace, with a current of 250 to 300 amperes at 70 volts. The reaction is finished

[1] Joly: "Sur le Bore," *Compt. rend.*, 97, 456.

in six or seven minutes. After cooling the crucible, a black mass is obtained, having the appearance of graphite, having a metallic fracture, and looking as though it had begun to fuse. After prolonged treatment with fuming nitric acid the substance is disintegrated and a crystalline powder remains which is treated six times with potassium chlorate and concentrated nitric acid. It is washed with water and dried.

(2) *Preparation by Solution in Iron Boride.*—Iron combines easily with boron and forms a definite boride which we have described. When an excess of boron and carbon are added to iron, and the whole heated in the electric furnace under the preceding conditions, a fusion is formed having a bright fracture. After treatment with aqua regia, the metal leaves a residue almost entirely formed of carbon boride. In this case, the crystals are poorly formed; after six treatments with potassium chlorate, they do not contain graphite, and their analysis leads to the formula B_6C.

(3) *Preparation by Solution in Copper and Silver.*—Iron dissolving with ease a great excess of boron, we sought to use in this preparation metals which at the moment of cooling do not form definite combinations with this non-metal. Silver and particularly copper gave the best results.

Carbon boride, obtained in silver, after treating the metal with nitric acid, is of great purity, but its crystallization is poor. From copper, bright, well-formed crystals are obtained.

An intimate mixture of boron and sugar carbon is prepared (boron 66, carbon 12), and 15 grams of this mixture are placed in a carbon crucible with 150 grams of coarse copper filings which are quite pure.[1]

The heating lasts for six or seven minutes with a current of 350 amperes at 70 volts. A little later, a malleable fusion is found in the furnace, which has the appearance of metallic copper slightly blackened on the surface. The fusion takes place very rapidly, and the quantity of copper fusions necessary to give 200 grams of carbon boride can be obtained in three hours.

A simple treatment with ordinary nitric acid gives the well-

[1] Care should be taken to avoid the presence of sand in these copper filings, as it gives crystalline carbon silicide.

crystallized boride, which contains only a small quantity of graphite. To separate the latter, it is treated six or eight times with a mixture of dry potassium chlorate and concentrated nitric acid, then with boiling sulphuric acid for several hours. It is finally digested again with the mixture of chlorate and nitric acid, washed with water and dried.

Properties.—This carbon boride belongs to the same class of compounds as carbon silicide. It possesses, like it, great stability and great hardness; the carbon boride appears in bright, black crystals having a density of 2.51 Chlorine attacks it below 1000° without evolution of light as shown by Joly. Boron chloride is formed, and a residue of very bright, porous carbon remains. Bromine and iodine are without action.

Heated to 500° in oxygen, no carbon dioxide is given off, but at 1000° it burns slowly with more difficulty than the diamond, giving carbon dioxide and a black residue covered with fused boric acid.

Sulphur does not act on carbon boride at the temperature of the softening of glass; the same is true with phosphorus and nitrogen at 1200°. The compound is not attacked by any of the acids, concentrated hydrofluoric acid, concentrated nitric acid or a mixture of both are without action at boiling. Heated in a sealed tube to 150° with fuming nitric acid, it loses nothing. Concentrated solutions of iodic and chromic acid are without action either boiling or in sealed tubes heated to 150°. At dull redness it is attacked by fused potash and by a mixture of the fused carbonates of sodium and potassium. The most curious property of this compound is its great hardness; while carbon silicide polishes the diamond only with difficulty without being able to scratch it, it has been possible for us to cut faces on a diamond with powdered carbon boride.

This compound is very friable; it can be obtained in a very fine powder in a new steel mortar and, mixed with oil, can be used instead of diamond dust on the steel wheel to cut the diamond. The hardness of this boride appears to be less than that of the diamond since the wear is slower, but the faces are cut clearly. It, with titanium carbide, is the first example of a definite com-

pound to act on the diamond. The hardness of this body is then much greater than that of carbon silicide.

Analysis. DETERMINATION OF CARBON.—We determined the carbon by two different methods:

(1) By treating the substance with chlorine, then heating the boat in a current of hydrogen, and finally burning the carbon in a current of oxygen, the weight of the carbon dioxide gave the content of carbon.

(2) A definite weight of carbon boride was mixed with lead chromate in large excess and heated to a high temperature in a porcelain tube. The carbon dioxide was collected and weighed, and gave the quantity of carbon.

ESTIMATION OF BORON.—Carbon boride was fused with a mixture of sodium and potassium carbonate in platinum crucibles, the fusion was taken up in water, nitric acid added, and the boron determined by methyl alcohol and lime, according to the method of Gooch,[1] using the apparatus which we have described.[2]

We obtained the following figures:

	1.	2.	3.	Theoretical.
Boron	84.57	84.19	84.52	84.62
Carbon	15.60	14.91	15.55	15.38

G. Glucinum Borocarbide

The existence of this compound prepared by Lebeau[3] is very interesting, inasmuch as it is an example of one of the double carbides which can probably be obtained in the electric furnace.

An intimate mixture of 75 parts pure glucina is made with 45 parts of boron and heated in a carbon boat in a furnace for tubes for seven to eight minutes with a current of 45 amperes at 950 volts. A very hard crystalline metallic mass is obtained. The halogens attack it in the cold as do the halogen acid gases. Oxygen only acts on it imperfectly as the boric acid formed impedes the reaction.

Analysis gave the following results:

	1.	2.	Theoretical for $Gl_8B_6C_4$.
Carbon	27.99	28.34	28.49
Boron	39.18	39.12	39.17
Glucinum	32.83	32.54	32.33

[1] Gooch: "Estimation of Boric Acid," *Am. J. Sci.*, **9**, 23 (1887).

[2] H. Moissan: *Compt. rend.*, **116**, 1087.

[3] Lebeau: *Compt. rend.*, **126**, 1147.

METALLIC PHOSPHIDES

Heretofore the definite combinations with phosphorus and the metals have been little known and poorly determined. The high temperature of the electric furnace has enabled us to obtain a number of these compounds which have definite formulas.

Phosphides of the Alkaline Earths

By causing the vapor of phosphorus to act on lime heated to redness, Paul Thénard obtained an amorphous product, cinnabar-red in color, whose composition corresponded to the formula CaP_2O.[1]

This body, which he called calcium phosphide, was decomposed by water, and this reaction established the existence and properties of the different phosphorus hydrides. Dulong has given a general method for the preparation of the phosphides, by the action of the vapor of phosphorus on the metal. These experiments were repeated by Virgier. The latter proceeding was not applicable in the preparation of calcium phosphide as the pure metal had not been known until our work.

Preparation of Crystalline Calcium Phosphide in the Electric Furnace.—Calcium phosphide can be obtained in the electric furnace by the reduction of tricalcium phosphate with carbon. The preparation requires some precautions on account of the relatively easy decomposition of calcium phosphide at the high temperature of the electric furnace. We first prepared pure tricalcium phosphate by precipitation. The compound, after drying, was heated in the Perrot furnace, then reduced to a fine powder and mixed with carbon in the following proportions:

Tricalcium phosphate	310
Lampblack	96

A small quantity of spirits of turpentine was added to the powder to form a paste and it was pressed into small cylinders. These were heated in a Perrot furnace in a lining of lampblack.

The intimate mixture of calcium phosphate and carbon was finally placed in the crucible of an electric furnace and submitted

[1] P. Thénard: "Sur les combinaisons du phosphore avec l'hydrogène," *Ann. Chem. Pharm.*, 14, 12 (1845).

for four minutes to the action of a current of 950 amperes at 45 volts.

On cooling, a fused mass was taken from the crucible; it should not adhere to the sides and it should not be heated too long. If it is heated too long the calcium phosphide will be contaminated on the outside with a small quantity of calcium carbide. On the contrary, if the heating is insufficient, the phosphide will be found to be mixed with fused phosphate which is not reduced and in which red crystals of the phosphide can be distinguished.

During this preparation in the electric furnace, only a small quantity of phosphorus vapors are evolved, but if the heating is continued, when reduction is complete, the calcium phosphide is decomposed, and phosphorus distils and burns in the vapors issuing from the furnace. The calcium finally unites with the carbon, and only calcium carbide remains containing a very small quantity of phosphide. Hence, when pure calcium phosphide is desired by this proceeding, it is important not to heat too long.

It is also possible to obtain fused calcium phosphide by heating in a carbon crucible in the electric furnace, the calcium phosphate of P. Thénard, prepared by the action of a large excess of phosphorus vapor or lime heated to redness. With an arc of 800 amperes at 50 volts, the fusion is made in seven or eight minutes. A dark red mass remains, which is contaminated with calcium carbide.

Properties.—Calcium phosphide prepared in the electric furnace appears in fragments having a red-brown color, similar to that of calcium nitride. It has a crystalline fracture and, when the reduction has not been complete, appears in good crystals of a red-brown color in the fused phosphate. Calcium phosphide is difficultly fusible; we have not been able to fuse it in the electric furnace. At the point where Bohemian glass softens, calcium phosphide is slowly dissociated into its elements *in vacuo*. The evolution of a small quantity of phosphorus vapor is quite distinct. The tension of dissociation reaches a few millimeters only. Its density at 15° is 2.51.

At 900° calcium phosphide is not perceptibly altered in an atmosphere of hydrogen. Chlorine does not act in the cold on

calcium phosphide, but when heated to about 100° the reaction commences and continues with evolution of a bright light. Calcium chloride is formed along with the vapors of phosphorus chloride. The action of bromine is in all points similar to that of chlorine, while the vapor of iodine attacks the phosphide about dull redness.

The combustion of calcium phosphide in oxygen takes place at about 300° with evolution of bright light. Lime is formed along with phosphoric anhydride. Sulphur attacks it at about 300°, decomposing it with great evolution of heat, producing a yellow sublimate and forming calcium sulphide. The action of nitrogen on calcium phosphide is particularly interesting. Nitrogen can drive out the phosphorus from this combination and form calcium nitride. It is known that calcium nitride is readily decomposed by water giving ammonia, a reaction which can be used in industry; but the heat of formation of calcium phosphide seems to be greater than that of the nitride, as all of our experiments below 900° were fruitless.

At 1200°, nitrogen acts partially on the phosphide, eliminating a small quantity of the phosphorus, but the reaction is far from being complete, and the residue when treated with water gives a mixture of ammonia and hydrogen phosphide, the latter being in great excess. A dissociation of calcium phosphide appears here.

Heated in the vapor of arsenic to the fusion of glass, calcium phosphide is not attacked.

Boron and carbon are without action at 700°. In the electric furnace, the phosphorus is entirely displaced.

The gaseous halogen acids energetically attack it. Hydrochloric acid reacts with evolution of light at redness.

At about 700° hydrogen sulphide has no apparent action; the same is true of ammonia gas.

The action of water on this body is characteristic. In contact with cold water, calcium phosphide is decomposed with formation of calcium hydroxide and hydrogen phosphide.

If the substance is in crystalline fragments the lime formed retards the reaction. On the contrary, if it is powdered, the reaction is violent.

When the phosphide has been sufficiently heated in the electric furnace, the hydrogen phosphide, which is formed in this decomposition by water, is not spontaneously inflammable in contact with air. This compound is then different from that prepared by P. Thénard. The decomposition is, however, somewhat complex, and all of the gas obtained is not PH_3. Some specimens that were less heated, gave with water hydrogen phosphide containing free hydrogen. On the contrary, if the phosphide has been heated to a high temperature, hydrogen is not given off, but a little acetylene is obtained.

The acids attack only the phosphide on account of the water they contain. Concentrated nitric acid scarcely attacks it in the cold and when heated the action is very slow. With ordinary nitric acid, it is rapidly oxidized in the cold; nitrous vapors are evolved along with a gas which inflames spontaneously.

Similarly fuming sulphuric acid does not attack the phosphide in the cold, while the decomposition is violent with dilute sulphuric acid.

Absolute alcohol, ether, benzene, and spirits of turpentine do not act at the ordinary temperature.

Oxidizing agents act violently, fused potassium chlorate and bichromate attack it with evolution of light. If a mixture of potassium permanganate and powdered calcium phosphide is gently heated, explosion takes place and light is evolved.

Nitrous and nitric oxide oxidize it in the cold with evolution of light. Lime is formed and a small quantity of nitride.

Analysis.—Calcium phosphide was decomposed by direct oxidation with fuming nitric acid. The calcium was precipitated as sulphate in presence of alcohol, and the phosphoric acid determined as magnesium ammonium phosphate.

We obtained the following results:

	1.	2.	3.	4.	Theoretical for Ca_3P_2.
Ca.....	65.82	65.71	65.38	65.40	65.93
P.....	....	33.79	33.92	33.85	34.06

Barium and Strontium Phosphides

Jaboirs,[1] by applying the above method, obtained barium and

[1] Jaboirs: *Compt. rend.*, **129**, 762.

strontium phosphides, by reducing the corresponding phosphates with carbon in the electric furnace. Barium and strontium phosphides have respectively the densities 3.18 and 2.68 and present all of the properties of calcium phosphide. Their analysis corresponds to the formulas Ba_3P_2 and Sr_3P_2.

Iron, Nickel, Cobalt and Chromium Phosphides

When an attempt is made to reduce, in the electric furnace, the phosphates of these metals, only phosphides of variable composition appear. Maronneau[1] has been able to obtain definite products by the action of copper phosphide on these elements.

Iron phosphide, Fe_2P, appears in bright needles, which have a gray-white color and are not attacked by any of the acids except a mixture of nitric and hydrofluoric. The fused alkaline carbonates act completely when the phosphide is finely powdered and permit an analysis to be made.

Nickel phosphide, Ni_2P, and cobalt phosphide, Co_2P, show about the same properties.

Chromium phosphide, CrP, prepared by fusing a mixture of chromium and copper phosphide in the electric furnace and treating with nitric acid, has a dull gray color, a graphitic appearance and, like the preceding, is not attacked by the acids and is completely destroyed by fusion with a mixture of nitrate and carbonate.

Copper Phosphide

By the direct action of phosphorus on copper a number of definite phosphides have been obtained. Maronneau,[2] by reducing copper phosphate with carbon, has obtained the body Cu_2P. A mixture of 400 grams of copper phosphate and 100 grams of petroleum coke are heated in the electric furnace with a current of 900 amperes at 45 volts. The fusion obtained is made the negative electrode in a cold saturated solution of copper sulphate. At the end of several days, a black, crystalline powder is obtained which, when washed with water, alcohol, ether, and dried, corresponds to the formula Cu_2P.

[1] Maronneau: *Compt. rend.*, **130**, 656.
[2] Maronneau: *Ibid.*, **128**, 936.

METALLIC ARSENIDES

Like the phosphides, the arsenides prepared by direct union or by reducing the arsenates have been poorly defined compounds. By reducing the arsenates with carbon in the electric furnace, Lebeau[1] has obtained well-crystallized arsenides of the alkaline earths corresponding to the series of phosphides.

Preparation of Calcium Arsenide

An intimate mixture of 100 parts of calcium arsenate and 30 parts of carbon is prepared, and sufficient spirits of turpentine are added to make a paste of the proper consistency. The mixture is then heated to drive off the volatile products, after which it is heated two or three minutes by a current of 950 amperes at 50 volts. A fused mass is obtained which contains calcium arsenide nearly always mixed with a little calcium carbide and graphite. This substance can then be prepared as readily as calcium carbide.

Properties.—Calcium arsenide appears as a fused mass having a crystalline texture. Pulverized and examined under the microscope, it appears in transparent particles which have a red-brown appearance, exactly resembling calcium nitride. Its density is 2.5 at 15°.

The compound is somewhat active chemically. Fluorine attacks it in the cold, chlorine about 200°. Bromine and iodine react with evolution of light below redness. Carbon has no action at 1000°, but in the electric furnace the arsenic is completely eliminated after ten minutes' heating. It is difficult to obtain the arsenide completely free from carbide.

Water gives a characteristic reaction, evolving pure hydrogen arsenide. This is an excellent method for the preparation of this gas.

Analysis gave the following figures:

	1.	2.	Theoretical for Ca_3As_2.
Calcium	45.18	44.83	44.44
Arsenic	55.83	55.17	55.55

[1] Lebeau: *Compt. rend.*, 128, 95.

Strontium and Barium Arsenides

Strontium and barium arsenides having the respective formulas, Sr_3As_2 and Ba_3As_2, are prepared in a similar manner. Like the calcium compound, they act on water evolving pure hydrogen arsenide. The other properties are not sensibly different from those of calcium arsenide.

METALLIC SULPHIDES

From the general standpoint of reactions at high temperatures it was interesting to study the action of the sulphides in the electric furnace. Mourlot,[1] by reducing the sulphates with carbon, has been able to prepare, in crystalline condition, lithium sulphide, the sulphides of the alkaline earths and magnesium, which were known before only in the amorphous state. The use of this method has led to the artificial preparation of some known crystalline sulphides as zinc, cadmium, lead, manganese, and antimony. Some of the sulphides volatilize readily in the electric furnace such as those of zinc, cadmium, lead and tin and crystallize on cooling. The other sulphides are, as a rule, dissociated and it is possible to obtain the free metal or the corresponding carbide when carbon is present.

[1] Mourlot: "Thése a'la Faculté des Sciences," Paris, 1899.

CONCLUSIONS.

The electric furnace which we have described at the beginning of this work has permitted the solution of a number of hitherto unsolved problems. With its aid we have been able to saturate melted cast iron with carbon at 3500° and, by suddenly cooling it, obtain in the fusion the varieties of carbon having a density of 3.5.

We have been able to prepare the black and transparent diamond; the latter in regular octahedrons, in cubes, in fragments having a distorted crystallization, in drops, in crystals which break, either transparent and perfectly clear or with black dots, such as are found in nature. These crystals, although small, are in all points similar to those found at the Cape or in Brazil.

It has been possible to show that at the ordinary pressure, boron and carbon pass from the solid to the gaseous state without becoming liquid. On the contrary, under the action of a great pressure, carbon becomes liquid, its density increases and it gives the diamond.

By means of the electric furnace, we have been able to bring all the forms of carbon to graphite, the variety stable at 3000° at the ordinary pressure. After a study of the different graphites, we have shown that the stability of these forms of carbon is a function of the temperature to which they have been heated; finally, we prepared the swelling variety.

By removing the limit of temperature to which we can submit the different bodies in the laboratory, we have been able to enter upon new physical investigations on the fusion and volatilization of some elements and compounds.

We have fused with ease, lime, manganese, molybdenum, tungsten, vanadium, and zirconium. By using a more intense current we have volatilized in large quantities silica, zirconia, lime, aluminum, copper, gold, platinum, iron, uranium, silicon, boron, and carbon, and obtained crystalline metallic oxides.

This elevation of temperature has permitted us to make general some reactions which were hitherto regarded as limited by reason of the insufficience of our means of action.

In the electric furnace, barium and strontium carbonates are reduced to carbon dioxide and baryta and strontia. The oxides which have been regarded as non-reducible have been reduced. We have reduced by carbon, alumina, silica, the oxides of the alkaline earths, the oxides of uranium, vanadium, and zirconium. The reductions by carbon, which were difficult to obtain in the wind-furnace, were made in a few minutes in our apparatus. I give as example the preparation of manganese, chromium, tungsten and molybdenum. And, since at this high temperature, the refractory metals become liquid, it is easy to avoid the action of oxygen and nitrogen and to obtain them in a very pure state. Frequently, it is true, they are combined with carbon, but it is an easy matter to refine them by a second fusion and to obtain ingots, some of which do not scratch glass and can be filed.

These preparations can be made in large masses. Very often our crucibles contained 1000 to 1200 grams of oxide to be reduced; the yield under these conditions becomes important, and it was by kilograms that our laboratory samples were obtained.

These facts have made it possible for us to study under new conditions, chromium, manganese, molybdenum, tungsten, uranium, vanadium, and zirconium.

When strong currents are used in these experiments, the formation of impurities which cannot exist at these high temperatures is frequently avoided. I mention, as example, the preparation of fused titanium, which can be obtained free from nitrogen when a current of 1200 amperes at 70 volts is used. On the contrary, with a current of 400 amperes at 60 volts, only titanium nitride can be prepared.

We think that these investigations present numerous applications. Our different methods of preparation can readily enter into practice, and metallurgy can be aided. It must not be forgotten that the refractory metals which are readily obtained in the electric furnace, can also be prepared alloyed with aluminum, as we have shown, when their oxygen compounds are reduced by this metal. The alloys of aluminum with these metals can be used to obtain the refractory metals, since the excess of aluminum can be easily removed.

This new method of preparing alloys and as well the electric furnace enables us to obtain metallic baths under well-determined conditions. A number of refractory metals will probably afford interesting alloys. The electric furnace permits the study of many new series of crystalline compounds. We speak of the borides, silicides and carbides.

These compounds have very simple formulas; at a very high temperature only a single combination is frequently obtained.

The chemistry of high temperatures is a very simple chemistry.

The silicides are bodies of great hardness; some, like those of boron and titanium, can be used to cut the diamond.

Certain fused metals are without action on carbon at their boiling temperature, for example, gold and bismuth.

Others dissolve carbon at this high temperature and subsequently separate it as graphite below their point of solidification, as the members of the platinum group.

Finally, a large number of metals form definite and crystalline compounds with carbon. These carbides can be divided into two classes. The first contain the bodies which decompose water in the cold, as the carbides of the alkalies and alkaline earths, the carbides of aluminum, glucinum, cerium, lanthanum, thorium, etc. The second is formed of stable carbides as chromium, molybdenum, tungsten, and titanium.

The carbides, decomposed by cold water as we have shown, give only a single hydrocarbon in a very pure condition, as lithium, calcium and aluminum; others as manganese, a mixture of hydrogen and methane; still others, as thorium, a more complex mixture of acetylene, methane, ethylene and hydrogen. But the most curious phenomenon is the decomposition in presence of water given by the cerium and uranium carbides. In this case, not only is there formed a mixture of gaseous hydrocarbons, but also liquid and solid hydrocarbons.

These new reactions evidently play great part in the geological formation of natural hydrocarbon gases, the schists, and petroleum. Possibly by their aid, they also explain the manifestation of volcanic centers accompanied by emanations of gaseous, liquid,

and solid hydrocarbons. Finally, these carbides must have great importance in the first heat reactions which proceeded on the surface of the earth.

The carbon of all actual organic compounds must have been combined originally with metals as metallic carbides. It is probable that these compounds still appear in the stars at high temperatures. We would add that in the same period, nitrogen would be found as metallic nitrides, while hydrogen very likely existed in large quantities in a pure state, in a gaseous atmosphere containing few hydrocarbons and cyanogen compounds. The electric furnace appears to bring back the conditions of this geological epoch.

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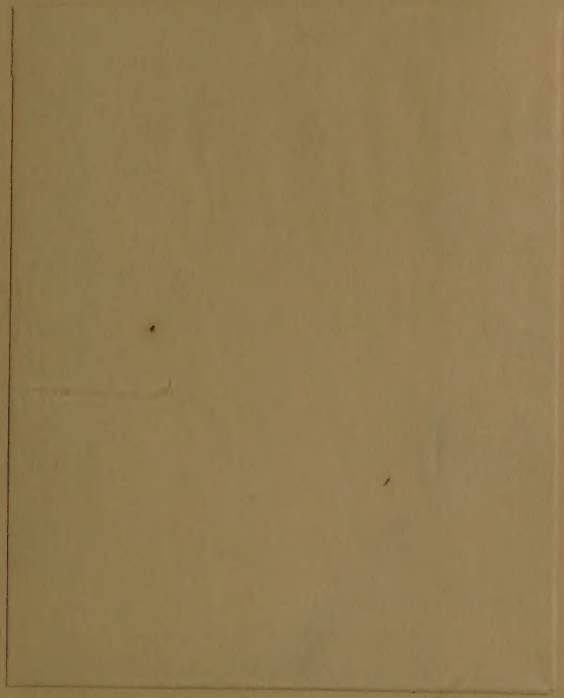

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